A Mechanistic Study on the Coupled Organic and Colloidal Fouling of Nanofiltration Membranes

by

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Abstract

The more wide-spread use of nanofiltration membranes in industrial applications is dependent upon understanding the fouling behavior of representative feed solutions, such as complex suspensions with both organic and colloidal inorganic foulants. In this thesis, three hypothesized mechanisms responsible for enhanced membrane flux decline in the presence of multiple foulant types are examined experimentally: increased hydraulic resistance of the mixed cake layer structure, hindered foulant diffusion due to interactions between solute concentration polarization (CP) layers, and changes in colloid surface properties due to organic adsorption. Additionally, a modified composite cell-model is developed to incorporate the structural differences of a merged, combined fouling layer. Results, including a synergistic effect caused by increased resistance of a heterogeneous fouling layer as well as the adsorption effects of interacting foulants, indicate that current fouling layer models need to be reexamined to include the mechanisms suggested in this study.
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1. Introduction

Limited natural freshwater resources coupled with increasing global population have created a worldwide demand for safe drinking water. As populations flourish in areas of limited natural water resources and existing freshwater sources become overstressed, drinking water treatment technologies that produce clean water from non-traditional sources, such as salty and brackish waters will also grow in demand. Due to their high multivalent ion and organic contaminant rejection rates, nanofiltration and reverse osmosis are some of these promising technologies. One intrinsic problem in membrane filtration is that substances retained on the feed water side of a membrane build up on the membrane surface, resulting in a decrease in clean water productivity which can be measured by a decrease in permeate water flux. Any decrease in permeate water flux is referred to as membrane fouling. Fouling can cause substantial increases in operation costs as increased pressures are needed to maintain clean water production rates, ultimately limiting the more widespread use of membrane technologies.

Performing laboratory and pilot scale experiments under solution conditions similar to those of natural waters and wastewaters likely to be treated using membrane technology aid in understanding how these membranes will perform during application. By developing mathematical models based on the physical fouling mechanisms, flux decline can be predicted before it happens. Understanding these fouling mechanisms and the ensuing flux decline can lead to the development of more effective pretreatment & cleaning methods. However, the more limited the solution conditions tested are in such flux decline models, the more restricted the scenarios are to which the research conclusions can be applied. Traditionally, most membrane experiments and fouling
models focus on understanding and predicting the fouling that occurs when only one type of foulanant is present in solution. However, multiple types of substances are likely present in natural waters and waste waters, changing how membranes might perform in real application. Not only will a poly-dispersed solution affect the fouling behavior of membranes by altering cake layer formation, but multiple substances present in a solution can also interact with each other, further complicating the potential fouling behavior. A deeper understanding of the fouling mechanisms controlling filtration of representative solutions of natural and wastewaters will lead to better fouling control mechanisms, cleaning techniques and perhaps the creation of anti-fouling membranes themselves.

1.1 Organization of thesis

The following chapters explain the details of this research and the conclusions that can be drawn from these studies. Chapter one introduces the purpose of this work. Chapter two presents a literature review of studies previously performed related to this topic, including: theories of colloidal and organic fouling, typical foulants found in natural and waste waters, factors affecting flux decline due to fouling, and the findings of previous experimental and modeling studies on combined fouling. Chapter three discusses the effect foulant-foulanant interactions have on combined fouling behavior. Chapter four discusses preliminary modeling results of a triple component-system developed to predict the fouling of a solution containing colloids, organic macromolecules and salt ions. Chapter five presents the general conclusions of this work and chapter six provides ideas for future work that could be done on this topic to extend current knowledge.
1.2 Statement of purpose

The purpose of this research is to more fully understand the mechanisms involved during the combined filtration of colloidal and organic substances using nanofiltration membranes, particularly focusing on how foulant-foulant interactions can affect combined fouling mechanisms. In order to achieve a thorough understanding, colloid-organic interactions must first be characterized and incorporated into the analysis of cross-flow filtration experiments. The second purpose of this research is to incorporate the mechanisms correlated to combined flux decline into a mathematical model in order to accurately predict flux decline of a complex solution.
2. Literature Review

2.1 Background on membrane technology

Membrane filtration is a promising water treatment technology that converts natural and waste waters into clean water using pressure driven flow. This technology has practical application in drinking water purification, desalination, wastewater recycling, water softening and the food processing industry. Membrane filtration is a separation process that purifies water by allowing water molecules to pass through the membrane barrier while suspended solids and other substances are caught on the membrane surface. Several different types of membranes used in liquid applications, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes, and the substances they filter are illustrated in Figure 2-1.

**Figure 2-1** Comparison of the substances filtered and the operating pressure range of different types of membrane filtration processes.
The figure shows the gradient of membranes from MF, membranes that have the largest pore-size that allows for the greatest passage of substances, to RO membranes, which do not have physical pores and only filter through diffusion. RO membranes can exclude all substances except for water molecules, making it a useful technology for desalination. Fig. 2-2 shows specifically what size range of foulant each membrane can filter and example foulants within that size range.

Figure 2-2 Separation size range of different membrane technologies.

Synthetic membranes used for drinking water treatment can be assembled of both organic and inorganic materials. Organic membranes account for the majority of membranes used (including those in this study) and are typically assembled from a polymer base, while inorganic membranes can be made of materials such as zeolite, aluminum oxide, or titanium oxide. Membranes can also vary in cross-sectional structure, from symmetric to asymmetric to thin-film composite structures, depending on the method used to cast the membrane. Membrane material and casting method is not
chosen arbitrarily but is based on specific factors of the given application and feed water solution characteristics [1]. In NF and RO composite membranes, a thin separation layer of polyamide is coated on a thicker structural support layer (polysulfone, for example) in order to provide higher rejection of ions in and dissolved materials in the thin separation layer while still being able to withstand high operating pressures with the structural support layer.

MF and UF configurations require minimal pretreatment steps due to their large pore sizes. However, due to increased rejection and consequent increased fouling potential, NF and RO membranes require more involved pretreatment steps. Generally, as membrane rejection increases an increase in operating pressure is also required (Fig. 2-1), which results in higher operating costs. The looser MF and UF membranes filter contaminants through size exclusion while tighter membranes (NF and RO) also employ Donnan exclusion (separation based on electrostatic repulsion).

In order to minimize operating costs and maximize clean water production, fouling can be minimized through modification to system conditions. Feed solution composition (i.e. pH, ionic strength, salt and organic composition, temperature), filtration geometry, operating pressure, and membrane characteristics (i.e. surface roughness, zeta potential, hydrophobicity) can all affect the fouling proclivity of a membrane (see section 2.2.4 Factors affecting membrane flux decline).

2.2 Membrane fouling

There are two main types of membrane fouling: reversible and irreversible fouling. The original permeate flux of a membrane fouled from reversible fouling can be recovered after system pressure is released and the necessary cleaning protocol (such as
backwashing or chemical cleaning) has been performed. Irreversible fouling causes a permanent decrease in membrane productivity through decreased permeate flux even after cleaning has been performed. Irreversible fouling will decrease the integrity of the membrane and reduce its lifetime.

In order to predict membrane permeate flux decline, a thorough understanding of all contributing fouling mechanisms is required. Membrane fouling occurs as a result of foulants being brought to the membrane surface and the interactions between the foulant and the membrane. Mechanisms leading to flux decline for loose membranes, such as MF and UF, include pore blocking (when foulants cover membrane pore surfaces) and pore constriction (when foulants reduce pore size by clogging pores). Concentration polarization and fouling layer formation are fouling mechanisms of all types of membranes. Fouling during NF and RO is often assumed to occur only on the membrane surface due to the tightness of NF and RO membranes and relative size of the foulants compared to membrane pore size [2].

Flux of clean water (m$^3$/m$^2$·s), $v_0$, through a membrane can be directly related to applied pressure across a membrane through Darcy’s equation:

$$v_0 = L_p \Delta P = \frac{\Delta P}{\mu R_m}$$

(1)

where $L_p$ is the permeability of the membrane (m/s·Pa), $\Delta P$ is the trans-membrane pressure (Pa), $\mu$ is the solution viscosity (Pa·s), and $R_m$ is the hydraulic resistance due to the membrane (m$^{-1}$). As long as clean water is being filtered, the relationship between flux and applied pressure will remain linear. In the presence of solutes (either salt ions and/or foulants), additional layers of resistance will form at the membrane surface as a
result of the rejection of these constituents. During these conditions, the resistance in series model expresses membrane permeate flux, \( v_w \), as:

\[
v_w = \frac{\Delta P - \Delta \pi_m}{\mu(R_m + R_{cp} + R_f)}
\]  

(2)

where \( \Delta \pi_m \) is the change in osmotic pressure across the membrane (Pa) due to rejection increasing the concentration of salt ions and \( R_{cp} \) and \( R_f \) are the hydraulic resistances due to the foulant concentration polarization (CP) layers (of both salt ions and foulant particles) and the fouling layer (formed from the rejection of the foulant) (m\(^{-1}\)), respectively.

Concentration polarization is the phenomenon in which the solute or particle concentration in the vicinity of the membrane surface is higher than that in the bulk [1]. Concentration polarization is a form of reversible fouling, disappearing as soon as the system pressure is released, and is determined by three transport mechanisms. These mechanisms include: convective permeate flow as transport to the membrane surface, diffusion as back transport away from the membrane surface, and convective tangential flow as transport along the membrane surface [1]. Back transport through diffusion incorporates Brownian diffusion, shear-induced diffusion, and/or inertial lift (where for particles \( \ll 1\mu m \), shear-induced diffusion and inertial lift are negligible) [3]. Solute transport within the CP layer is often described with the convective diffusion equation:

\[
\frac{\partial C}{\partial t} + \mathbf{v} \cdot \nabla C - \nabla(D \nabla C) = 0
\]  

(3)

where \( D \) is the back diffusion coefficient, \( \mathbf{v} \) is the permeate flow velocity and \( C \) is the concentration of the solute. In the presence of a complex suspension, the diffusion term
may be completely different from that when a single non-interacting foulant is present due to solute-solute interactions (see Theory, Chapter 3 and Theory, Chapter 4).

2.2.1 Typical natural and wastewater foulants.

Feed streams treated by membrane filtration can contain a variety of suspended and dissolved substances depending on the geographical region and source of the water being treated. Typical foulants can be divided into four main categories: suspended inorganic colloids, dissolved organic macromolecules, inorganic precipitates, and biofoulants (including extracellular polymeric substances or EPS). Colloids are ubiquitous in natural and waste waters and can vary in size from a few nanometers to a few micrometers. Aquatic inorganic colloids consist of clay minerals, colloidal silica, silicates, as well as iron, aluminum, and manganese oxides [4]. Natural organic matter (NOM) and humic substances are major organic foulants present in natural surface waters, while proteins and polysaccharides are found in larger concentrations in waste waters [5]. Additionally, emerging organic micro-pollutants present at very low concentrations in waste waters (endocrine disrupting compounds (EDCs) and pharmaceutically active compounds (PhACs)) are receiving much attention due to their potential long-term health effects [6, 7]. Scaling of membranes is caused by inorganic components, such as CaCO₃ and CaSO₄, which complicate fouling by precipitating out of the feed stream and crystallizing on the membrane surface, forming hard mineral deposits [8]. Biofouling, the least well understood type of fouling for nanofiltration and reverse osmosis membranes, is the deposition or growth of microorganisms on the membrane surface that results in flux decline [9]. Fouling of solutions containing multiple types of
foulants is another situation that is relatively not well understood. Since individually their fouling mechanisms have been well characterized, this study focuses on the fouling caused by suspended colloids and dissolved organic macromolecules in combination.

2.2.2 Colloidal cake layer formation.

The fouling layer formed at the membrane surface during colloid filtration is commonly called a cake layer. Two approaches have been used to theoretically describe the formation of a cake layer. In the thermodynamic approach, or phase-transition model [10], concentration polarization transforms into a cake phase only after a certain critical concentration at the membrane surface is exceeded, depending on the pressure of the system and size of particle filtered [11]. This approach simplifies surface interactions [12] and the effect of physical chemical properties of the colloids and membrane surface by assuming that once the critical concentration is reached, all particles transported to the membrane surface deposit.

The other approach, a particle adhesion model, contends that the amount of particles that will deposit on the membrane surface is determined by a particle adhesion probability that considers surface roughness and particle size [13]. The major limitations of this model include the absence of particle or surface interactions during the calculation of particle adhesion probability, concentration polarization effects, and back transport mechanisms. Previous studies have clearly shown that fouling layer formation and membrane flux decline strongly depend on the interactions between the particle and membrane surface [14, 15].

Resistance attributed to the colloidal cake layer ($R_c$) through the equation
\[ R_c = \frac{\hat{R}_c m_p}{A_m} \]  (4)

where \( R_c \) is the specific resistance of the colloidal cake layer, \( m_p \) is the mass of particles deposited on the membrane, and \( A_m \) is the membrane area. The specific resistance can be approximated using the properties of spherical particles through the Carman-Kozeny equation [16],

\[ \hat{R}_c = \frac{180 \mu (1 - \varepsilon)}{\rho_p d_p^4 \varepsilon^3} \]  (5)

where \( \varepsilon \) is the porosity of the cake layer, \( \rho_p \) is the density of the particles (kg/m³), and \( d_p \) is the particle diameter (m) [16]. This model assumes a hydraulic diameter and the empirical condition of almost touching mono-dispersed, incompressible spheres. Happel’s cell model can also model a mono-dispersed cake layer by mapping it to a single solid sphere located in a concentric spherical cell on which tangential stress is nullified [17]. Neither model accurately represents a complex solution with a distribution of particles of different surface characteristics.

2.2.2.1 Cake-enhanced concentration polarization.

The presence of a cake layer on the membrane surface can also create another fouling mechanism that contributes to an increased flux decline when solutes are present. The diffusive tortuosity caused by the porosity of a cake layer can hinder the back diffusion of the rejected salt ions, enhancing the concentration polarization effect of the solute and (through Eq. 2) decreasing the permeate flux [18, 19]. This effect is called cake-enhanced concentration polarization (CECP) or cake-enhanced osmotic pressure (CEOP) and is observable during filtration by an increase in salt rejection over time as...
salt concentration at the membrane surface increases. CECP is verified in other studies [20] yet is only a significant mechanism when the salt rejection of the membrane is relatively high (≅ 80%) [18].

2.2.3 Organic gel layer.

The fouling layer formed by organic macromolecules is often referred to as a gel layer. Complications arise when modeling gel layers since in addition to convective and diffusive mechanisms, adsorption onto the membrane surface is also involved. Consequently, gel layer formation is much less understood and models predicting flux behavior are mostly empirical or semi-empirical [21, 22]. Pore blocking and pore constriction are also organic fouling mechanisms that only contribute to flux decline during MF and UF [22].

2.2.4 Factors affecting membrane fouling.

Fouling behavior is mainly influenced by three factors; hydrodynamic conditions at the membrane surface, membrane surface characteristics, and feed solution characteristics (including foulant characteristics and solution conditions).

2.2.4.1 Hydrodynamic conditions.

Filter geometry is very important during membrane processes, as hydrodynamic conditions determine particle accumulation and fouling layer formation on the membrane surface, which in turn affects resistance and flux decline. Spiral wound, hollow fiber, plate and frame set-ups are all used in industrial application. Incorporating spacers into membrane systems (such as the spiral wound set-up) is another way to enhance surface
hydrodynamics. While all three configurations can include cross-flow dynamics, spiral wound and hollow fiber membranes have the additional advantage of maximizing membrane filtration area through radial filtration through a tube-like membrane. Seen in Fig. 2-3, a cross-flow configuration utilizes tangential dynamics along the surface of the membrane, while a “dead-end” configuration only allows for flow through the membrane (perpendicular to the membrane).

**Figure 2-3** Comparison of cross-flow vs. dead-end filtration.

The advantage of cross-flow filtration over dead-end filtration is that accumulation of particles on the membrane surface is reduced [23]. Cross-flow filtration creates shear effects on the surface of the membrane that can help alleviate the formation of thick fouling layers. In cross-flow configurations, the retentate (concentrated water retained by the membrane) can also be recycled back to the beginning to be filtered again, whereas in dead-end filtration the fluid exposed to filtration is limited by permeate flux.

In addition to cross flow rate, operating pressure and permeate flux can also have an impact on fouling behavior [24-26]. Higher operating pressures result in higher convective transport of foulants, increasing permeate flux through the membrane [24].
However, high operating pressures also has the adverse effect of creating higher permeation drag force and more compressed fouling layers that may counteract the advantage the higher permeate flux produces [25].

2.2.4.2 Membrane characteristics.

Nanofiltration membranes are best characterized according to hydrophobicity, surface roughness, surface charge, molecular weight cut-off (MWCO), permeability, and porosity of the thin outermost layer [2, 27, 28]. The hydrophobicity of nanofiltration membranes is one of the most influential factors in membrane fouling [28]. A large portion of fouling is thought to be caused by organic components that adsorb on the membrane surface via hydrophobic interactions. If the membrane surface charge is large enough to override the hydrophobic interactions, electrostatic attraction or repulsion forces between charged foulant components and the membrane surface can also influence the degree of fouling [26].

Colloidal fouling has been shown in most studies to correlate to the roughness of the membrane surface [29, 30]. Rough membranes exhibit ridge-and-valley structures that preferentially transport colloids into the valleys (where there is the least resistance) causing a more severe flux decline than smooth membranes in the presence of small colloids [31]. Surface roughness also affects fouling layer morphology, with smooth membranes producing a denser fouling layer than rough membranes, where fouling layers are more open [32]. Membrane permeability can govern flux decline by allowing a faster flow through the membrane. This increased permeate flux rate brings more foulants to the membrane surface, resulting in faster cake layer growth [2].
2.2.4.3 *Feed solution characteristics.*

Fouling behavior is often dependent on the type of foulant being filtered as characterized by its surface charge, molecular weight, particle size, or hydrophobicity. Solution conditions (i.e. pH, salt ion type, and ionic strength) can affect foulant characteristics and how foulants interact with each other and the membrane surface. Fouling is the greatest during filtration of solutions that have conditions in which foulant molecules are the least stable and exhibit the weakest attractive interactions [33, 34]. For example, hydrophilic uncharged dissolved foulants exhibited the least fouling at neutral pH, while negatively charged components perform better at high pH [28]. Additionally, organic foulant experiments performed with bovine serum albumin (BSA) on reverse osmosis membranes show that fouling of solutions with a pH close to BSA’s iso-electric point (IEP) created the greatest fouling flux decline due to aggregation caused by weakened electrostatic repulsion of the BSA molecules [34]. High ionic strength solutions enhance double layer compression and charge-shielding effects, leading to weaker electrostatic repulsion, also creating more rapid fouling conditions [34]. Solution chemistry can also affect the charge and configuration of organic molecules, such as natural organic matter (NOM). Calcium ions have been shown to significantly enhance fouling in the presence of NOM by forming complexes which result in highly compacted fouling layers and thus more severe flux decline [20, 24, 33].

The strength of the intermolecular adhesion forces between bulk foulants and the membrane surface has been shown to control the rate of fouling [15]. Furthermore, the strength of the foulant-foulant interactions also plays a key role in determining the rate and extent of organic fouling [14]. In a study by Lee and Elimelech (2006) [14], it was
found that stronger intermolecular adhesion forces between organic foulants existed under conditions of low pH, high ionic strength and in the presence of calcium ions.

2.3 Filtration of complex solutions

There exist several relevant experimental and modeling studies that seek to better understand the fouling behavior of during filtration of complex solutions. Here, a complex solution is defined as a solution containing multiple types of foulants of different physico-chemical properties (either size or surface characteristics).

2.3.1 Experimental studies.

Experimental studies observing the combined fouling effect of colloids and organic macromolecules on NF and RO membranes are limited in number and scope. Additionally, conflicting results have been observed. In Lee et al. (2005) [20], a combined solution of silica colloids and natural organic matter (NOM) was filtered under different salt conditions on a high salt-rejecting NF membrane. Flux declines of the combined fouling experiments were compared to the additive sums of the individual (either colloid or NOM in solution alone) flux declines to expose a synergistic effect. Under several salt conditions – including differing concentrations of NaCl and the presence and absence of CaCl₂ – combined fouling experiments show a faster deposition of foulants initially, but a lower flux decline than the additive sum in the latter stages of fouling. This reduced fouling during combined filtration compared to the additive sum was determined to be from a diminished effect of cake-enhanced concentration polarization (CECP) on the NOM stabilized colloids. In combined solutions containing
Ca$^{2+}$, the reduction is attributed to reduced NOM-calcium complexation due to competition between colloidal particles and NOM molecules for calcium ions.

In a similar study done by Li et al. (2006) [35], solutions containing both silica colloids and Suwannee River humic acid (HA) were filtered using a low salt-rejecting NF membrane. Using the same comparison described earlier, the combined fouling experiments this time revealed a synergistic fouling effect present during the entire length of the fouling experiments. Because these experiments were performed on a low salt-rejecting membrane, the effect of CECP was not significant and could not be credited as the combined fouling mechanism. Instead, the synergistic behavior was attributed to the hindered back diffusion of the foulants caused by the interaction between the organic and colloid, resulting in a more substantial deposition on the membrane surface.

2.3.2 Modeling studies.

Several mathematical models have attempted to predict the flux decline of poly-disperse solutions. A semi-empirical model developed by Dharmappa et al. (1992) [36] predicts the fouling of MF and UF membranes during filtration of a poly-dispersed colloidal suspension by assuming that particle accumulation on the membrane surface is governed by deposition and re-suspension of the particles and using mass transport and mass balance equations. Limitations of this model which would prevent its use in modeling NF and RO processes include assumptions of a completely mixed layer (which is likely not the care for all of filtration), incomplete incorporation of back transport mechanisms, omission of the concentration polarization effect, and the necessity of fitting data due to the empirical nature of the model
A more advanced approach combines the classical filtration theory with the concept of a particle cut-off diameter (under which particles deposit on the membrane) to predict filter cake thickness as a function of time [37]. This approach assumes an incompressible cake of discrete layers, stratified by average particle size, with the layer consisting of the greatest particle size adjacent to the membrane and the lowest in the outermost layer. The model predicts that as trans-membrane pressure is increased, the deposition of smaller particles increases average specific cake resistance. An analytical method by Kim and Ng (2007) verifies this phenomena by showing that a normal distribution of particle sizes will always exhibit a fouling layer with greater cake resistance (as compared to that of a log-normal distribution) due to the larger number of smaller particles in the normal distribution [38].

A predictive model by Baruah et al. [39] anticipates that in a poly-disperse suspension of colloids and macromolecules flux will be limited by the particle size causing the lowest permeate flux. Using this determined flux, the concentration of each species in the filter cake is back-calculated out to determine the equilibrium concentrations at the membrane wall. Packing densities are explored based on known particle sizes until packing constraints are satisfied and then flux is evaluated. Experimental results show that despite not incorporating particle interactions, microfiltration of a poly-disperse solution of macromolecules was accurately predicted [40].
3. Combined Fouling of Nanofiltration Membranes:

Mechanisms and Effect of Organic Matter

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3.1 Abstract

The accurate prediction of nanofiltration membrane performance in industrial applications is dependent upon understanding the fouling behavior of representative feed solutions. However, most membrane studies focus on fouling of a single type of foulant, which is not a good predictor for realistic feed solutions that contain multiple foulant types. In this study, combined fouling by organic and inorganic colloidal foulants is studied. Through the use of model foulants, three hypothesized mechanisms responsible for the enhanced membrane flux decline in the presence of multiple foulant types are examined: increased hydraulic resistance of the mixed cake layer structure, hindered foulant diffusion due to interactions between solute concentration polarization layers, and changes in colloid surface properties due to organic adsorption. All three mechanisms were found to play a role in combined fouling to various degrees. Organic adsorption was shown to cause the greatest synergistic effect. The synergistic effect caused by increased resistance of a heterogeneous fouling layer indicates that current fouling layer models need to be reexamined to include the suggested mechanisms.

Key words – Nanofiltration, combined fouling, foulant interactions, colloids, organic foulant

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3.2 Introduction

Nanofiltration (NF) is an attractive technology for producing clean water from non-traditional sources, i.e. brackish water and wastewater, since it can provide high multivalent ion and organic contaminant rejection at a much lower operating pressure than reverse osmosis. Unfortunately, as with all membrane filtration processes, an inherent problem of NF is decreased productivity due to fouling of the membrane by colloidal materials, dissolved organics, inorganic precipitates, and microorganisms. While fouling can be controlled by using low fouling membrane materials [29, 41-43], pre-treatment of the feed stream [44-47], and optimizing the system configuration and operation [18, 33], proper use of these control strategies still requires a deeper understanding of the responsible fouling mechanisms.

Most previous studies on membrane fouling have focused only on a single, well characterized foulant of homogenous physico-chemical properties (referred to in this paper as individual fouling). One marked limitation in applying the theoretical and experimental results obtained from these studies to water and wastewater filtration systems is that fouling in these systems is almost always caused by more than one type of foulant with various particle sizes and surface characteristics, most commonly both colloidal materials and dissolved organic macromolecules, e.g., natural organic matter (NOM) and soluble microbial products. Several studies have identified that poly-dispersed suspensions form cake layer structures with resistances different than mono-dispersed solutions and that interactions that occur between foulants be correlated to flux decline behavior [14, 36, 37, 48].
A limited number of studies on combined fouling (i.e., fouling with multiple types of foulants) by both inorganic colloids and dissolved organic matter have shown that fouling behavior differs under varying solution conditions and with different membrane types [20, 35, 49]. Li et al. [35] performed combined fouling experiments with a low salt-rejection NF membrane in the presence of silica colloids and NOM. Flux decline measurements revealed significantly faster membrane fouling in combined fouling experiments than what might be predicted by summing the contributions from each foulant based on the individual fouling experiments. The aggravated membrane fouling or enhanced flux decline, referred to as a synergistic effect, was attributed to the hindered back diffusion of each foulant. In another study performed on a high salt-rejection NF membrane, Lee et al. [20] found that flux decline during filtration of a mixture of NOM and silica colloids was initially greater than the sum of the flux declines caused by each foulant individually, but was reduced in the latter filtration stages. It was hypothesized that an “active salt rejecting layer” formed during combined fouling negated the effect of cake-enhanced concentration polarization (CECP), which increases the salt concentration and consequently the osmotic pressure in the concentration polarization (CP) layer of salt ions [18, 19]. It is important to note that although fouling behavior differed according to the experimental conditions of each study, common throughout these studies is the observation that combined fouling cannot be predicted from fouling by individual foulants alone.

The objective of this study was to understand the effects of different organic foulants found in water and wastewater on combined fouling during the nanofiltration of complex solutions containing both colloidal materials and dissolved organic matter.
Interactions of four model organic macromolecules with colloidal silica foulants and the membrane surface were thoroughly characterized and related to membrane flux behavior observed in cross-flow filtration experiments to reveal the different combined fouling mechanisms involved. Results of the study clearly demonstrated the significance of interactions among different foulant types, which has been largely neglected in previous mechanistic studies.

3.3 Theory

Three potential mechanisms have been identified as contributing to the combined fouling flux decline observed during previous combined fouling studies [20, 35, 49]. The weighted effect of each mechanism is anticipated to be different for interacting vs. non-interacting foulants.

3.3.1 Increased cake layer resistance.

Dissolved organic compounds in water and wastewater are much smaller in size compared to colloidal foulants such as silica. It has been shown that poly-dispersity in particle size distribution is likely to affect fouling layer resistance by altering the structure of the cake/gel layer formed at the surface of the membrane [37, 38, 50].

In the presence of either organics or colloids alone, fouling layer formation is governed by the resistance in series model,

$$v = \frac{\Delta P - \Delta \pi_m}{\mu(R_m + R_c)}$$

where $v$ is the permeate flux, $\Delta P$ is the applied pressure, $\Delta \pi_m$ is the trans-membrane osmotic pressure, $\mu$ is the dynamic viscosity of the solution, $R_m$ is the resistance of the
membrane and \( R_c \) is the resistance of the cake/gel layer. \( R_c \) is determined by the specific resistance of the fouling layer or the fouling layer mass per membrane unit area (\( \tilde{R}_c \)).

For mono-dispersed, spherical colloids, the specific cake resistance is usually estimated using the Carman-Kozeny equation,

\[
\tilde{R}_c = \frac{180 \mu (1 - e_c)}{\rho_p d_p^2 e_c^3}
\]

where \( e_c \) is cake layer porosity, \( \rho_p \) is solid density of the particle, and \( d_p \) is particle diameter. The Carman-Kozeny equation predicts that decreases in cake porosity and particle diameter result in an increase in the specific cake layer resistance. Although this equation is only applicable for rigid, nearly touching particles, one can imagine that as the porosity of the layer decreases due to the presence of smaller particles filling interstitial pore spaces, as shown in Fig. 3-1, for the mixed fouling layer adjacent to the membrane the same relation would be true. Fouling layer resistance would consequently increase, resulting in increased flux decline. A recent analytical study verified this theory by showing that a cake layer composed of normally distributed particle sizes will always create a higher specific resistance compared to a log-normal distribution with the same mean particle size due to the presence of more small particles in the normal distribution [38].

### 3.3.2 Hindered back diffusion.

The back diffusion of one foulant type may be hindered by the presence of the concentration polarization of fouling layer of other types of foulants. During filtration, permeate flow brings the solute towards the membrane surface, convective flow
transports the solute along the membrane surface tangentially and Brownian diffusion and shear-induced diffusion simultaneously transport the solute back to the bulk fluid. Recently, the Brownian and shear-induced diffusion phenomena were unified using irreversible thermodynamics [51]. For small particles (<< 1 μm), such as the colloidal particles used in this study, shear-induced diffusion is negligible [3]. Accumulation of the solute within the concentration polarization layer can be described by the convective-diffusion equation,

\[ \frac{\partial C}{\partial t} + \vec{\nu}_w \cdot \nabla C - \nabla (D \nabla C) = 0 \] (3)

where \( D \) is the back diffusion coefficient, \( \vec{\nu}_w \) is the flow velocity, and \( C \) is the concentration of the solute. A schematic description is available in Fig. 3-1.

The Stokes-Einstein equation (Eq. 4) can be used to estimate the diffusion coefficient of small, spherical solutes in free solution

\[ D_0 = \frac{k_B T}{3 \pi \eta d_p} \] (4)

where \( k_B \) is the Boltzmann constant and \( T \) is absolute temperature. When there is significant accumulation of colloids at the membrane surface, i.e. formation of a cake layer, back diffusion of smaller solutes, e.g., dissolved organic foulants, is hindered by the presence of the cake-layer due to the tortuous pathway of transport. The hindered diffusion coefficient is related to the porosity (\( \varepsilon \)) and tortuosity (\( \tau \)) of the cake layer [19].

\[ D^* = \frac{D_0 \varepsilon}{\tau^2} \] (5)

The slower back diffusion leads to faster accumulation of the smaller solutes and hence a higher concentration in the CP layer. This phenomenon has been demonstrated with salt
ions - termed cake-enhanced concentration polarization (CECP) - and has been identified as a significant contributor to membrane flux decline observed in colloidal fouling of NF and RO membranes [18, 19]. CECP is observed by a decrease in the observed salt rejection over time as the concentration of salt at the membrane surface increases.

CECP may also occur for dissolved organic compounds that are small enough to penetrate the colloidal cake layer. As a result, the concentration of dissolved organic foulants in the CP layer is increased and formation of the organic gel layer is accelerated. Meanwhile, the higher organic concentration in the CP layer increases local fluid viscosity. Although only valid at dilute concentrations, the Stokes-Einstein equation predicts that the diffusivity of colloids will be reduced as the local fluid viscosity increases, further accelerating colloidal foulant accumulation at the membrane surface. In reality, higher concentrations at the membrane surface will make colloid-colloid interactions and volume exclusion more important.

3.3.3 Alteration of colloid surface properties due to adsorption of dissolved organic macromolecules.

Adsorption of dissolved macromolecules on colloidal surfaces can disturb electric double layer interactions and alter van der Waals forces among colloids and between colloids and membranes, as well as cause steric hindrance effects. A number of studies on colloidal transport in porous media have shown that NOM can play an important role in facilitating the transport of natural and model colloids [52-54] and their aggregation kinetics [55]. Additionally, interactions between the organic foulant and the membrane surface can modify membrane surface properties, including membrane surface roughness,
hydrophobicity and charge, and has been shown to affect flux behavior [31, 34, 56, 57]. These changes can significantly modify the fouling behavior of colloidal particles by either increasing or decreasing (depending on the molecular characteristics of the organic foulant) colloidal aggregation in the CP layer and their deposition on the membrane surface.

3.4 Materials and Methods

3.4.1 NF Membrane.

A low-salt-rejection thin-film composite nanofiltration membrane (NF 270 by Dow-FilmTec, Minneapolis, MN) was used in all filtration experiments. Precut membrane samples were stored in de-ionized water at 4 °C. The storage water was replaced weekly. The hydraulic resistance of the NF 270 membrane, determined from clean water flux measurements, was 1.98 (± 0.09) × 1013 m-1 at 20 ± 0.3 °C. Observed salt rejection with 10 mM NaCl ranged from 40.2% - 58.8% at 20 ± 0.3 °C, consistent with the manufacturer’s specified salt rejection of 40-60%. Membrane surface zeta potential was characterized using a streaming potential analyzer (Zeta CAD, CAD Instrumentation, Les Essarts le Roi, France). Measurements were performed under the various solution conditions used in the filtration experiments. Before each measurement, the membrane coupons were soaked in 10 mM NaCl (the background electrolyte solution used in filtration experiments) for 24 hr at 4 °C. Membranes were then allowed to equilibrate with the test solution for 30 min before the measurement was started.
3.4.2 **Model foulants.**

Commercial colloidal silica, Snowtex-XL (ST-XL, Nissan Chemical America Corp., Houston, TX) was used as the model colloidal foulant. Manufacturer supplied data specified that particle size ranged from 40 to 60nm.

Humic substances, proteins and polysaccharides have been identified as the major organic foulants in water and wastewater [58-63] For this reason, four organic compounds were used in this study: Suwannee River humic acid (HA), dextran, sodium alginate, and bovine serum albumin (BSA). In addition to the other commonly studied organic foulants, dextran was chosen because it is known to have minimum interaction with most surfaces and can serve as a good model for “non-interacting” macromolecules. HA (standard II) was obtained from International Humic Substances Society (St. Paul, MN) and was not purified any further. Dextran from *Leuconostoc mesenteroides*, sodium alginate derived from brown algae, and BSA were purchased from Sigma-Aldrich (St. Louis, MO). The molecular weights reported by the manufacturers are 1 – 5, 9 – 11, 10 – 60, and ~ 66 kDa for humic acid, dextran, sodium alginate, and BSA, respectively. All stock solutions and feed waters were prepared using ultrapure water produced by a Millipore system (RIOS System, Billerica, MA). Because HA has low solubility under acidic conditions, pH was raised to 8.2 with NaOH and the solution was filtered using a vacuum filter (Whatman Grade No. 1 filter paper, England) and stored in an amber glass bottle. The concentration of the stock solution was then verified by total organic carbon (TOC) measurements with a TOC analyzer (Shimadzu Scientific Instruments, Japan). All stock solutions were stored in the dark at 4°C.
Surface zeta potential and hydrodynamic diameter of the model foulants were characterized by electrophoretic mobility and dynamic light scattering (DLS) measurements using a Zetasizer Nano ZS (Malvern Instruments, Westborough, MA).

3.4.3 Measurement of organic foulant adsorption on silica.

Adsorption of organic foulants on the silica colloidal particle surface determines their impact on colloid-colloid and colloid-membrane interactions. Adsorption of the model organic foulants on a silica surface was investigated using a quartz crystal microbalance with dissipation monitoring (QCM-D) technique (Q-Sense E4, Q-Sense, Glen Burnie, MD). Principles and applications of the QCM-D technique can be found elsewhere [64].

Silica-coated quartz crystals (QSX303, Q-Sense, Glen Burnie, MD) were used to simulate the surface of the model silica colloidal foulant. QCM-D measurements employed the same background solution (10 mM NaCl) and organic concentration (20 mg/L) used in the cross-flow filtration experiments. Before each experiment, the crystal sensors and the flow modules were cleaned with 2% sodium dodecyl sulfate (SDS) solution followed by de-ionized water and dried with ultrapure N₂ gas. The crystals were further cleaned in a UV/Ozone ProCleaner (BioForce Nanosciences, Ames, IA) for 20 min. In each experiment, fundamental frequencies of each crystal were first verified under dry air conditions. Then, a baseline was established by running the background solution (10 mM NaCl) for 10 min. This was followed by the adsorption phase using the organic foulant solution. After adsorption equilibrium was established, the influent was
switched to the buffer solution again to remove the residual foulant solution in the cell channel.

3.4.4 Membrane filtration experiments.

Nanofiltration experiments were carried out in a laboratory scale cross-flow membrane filtration system consisting of two membrane-cells in parallel [65]. A pulsation dampener (Model H1020V, Blacoh Fluid Control, Inc, Riverside, CA) situated at the outlet of the hydra-cell pump was charged at 80% operating pressure to dampen pressure irregularities. Feed water temperature was kept constant at 20°C using a recirculating water chiller (VWR, West Chester, PA).

Filtration experiments included three main phases: membrane compaction, conditioning, and fouling. The membranes were first compacted at 100 psi (689.5 kPa), a pressure higher than the designed experimental pressure, using ultrapure water for a minimum of 5 hours to obtain a stable clean water flux. During the conditioning phase, background electrolyte solution, i.e. 10 mM NaCl was filtered through the membranes for at least 9 hours. Pressure was adjusted to yield a stable permeate flux of 2 x 10^{-5} m/s in all experiments, corresponding to an applied pressure range of 65 – 70 psi (448 – 483 kPa). This ensured the same initial permeate flux for the fouling stage of all experiments. Conductivity of both permeate and feed waters was monitored during the conditioning phase to check membrane integrity and establish initial observed salt rejection. After a stable permeate flux of 2x10^{-5} m/s and appropriate salt rejection had been achieved, the fouling phase was started by addition of the corresponding foulant or foulants. The pump was stopped while the foulant was introduced to the feed tank and allowed to mix
thoroughly for 5 min. before pumping was resumed. A sample was taken from the feed reservoir immediately before filtration was resumed for confirmation of foulant concentration. Concentrations of colloidal and organic foulants used were 100 mg/L and 20 mg/L, respectively, in both individual fouling and combined fouling experiments. Pressure, permeate flux, and feed water temperature were continuously monitored during the experiments. Samples were taken from both the feed and permeate at predetermined times during both the conditioning and fouling stages for analysis of pH, conductivity (Oakton pH/CON 510 Benchtop Meter, Oakton Instruments, Vernon Hills, IL) and foulant concentrations. Concentrations of organic foulants were determined by TOC measurements. Colloidal foulant concentrations in the feed were determined by turbidity measurements using a turbidity meter (Hach Company, Loveless, CO). The cross-flow system was thoroughly cleaned after each experiment with 6 L of 5 mM NaOH recirculated for 1 hr followed by three rinses with 6 L of de-ionized water for at least 1 hr each. All experiments were repeated at least twice.

3.5 Results and Discussion

3.5.1 Characteristics of model foulants.

The model foulants were characterized for their size and surface zeta potential under the solution conditions used in the filtration experiments. Table 3-1 summarizes the results of the characterization. The mean hydrodynamic diameter was derived from an average number-based-distribution based on at least 5 measurements. BSA has a negative surface zeta potential of -20.7 ± 0.9 mV under the experimental conditions used whereas that of dextran was close to neutral at -7.2 ± 1.5 mV. Alginate and HA had a
much more negative zeta potential, measuring -45.0 ± 1.2 and -37.9 ± 1.2 mV, respectively, under the same solution conditions.

The model inorganic foulant (ST-XL) measured 60.7 ± 1.2 nm in hydrodynamic diameter and had a high negative surface zeta potential (ζ = -37.9 ± 0.4 mV) under experimental conditions. These results agree with the manufacturer’s specifications of size (between 40-60 nm) and previously published zeta potential measurements [20]. The measured particle sizes of dextran, BSA and sodium alginate were all one order of magnitude smaller than that of ST-XL indicating that they can penetrate the ST-XL colloidal cake layer during filtration. Particle size is not reported for HA because it’s extremely small size (~1 nm) is beyond the detection range for DLS measurement.

3.5.2 Adsorption of organic foulants on silica surface.

QCM-D experiments were performed using silica-coated crystal sensors to investigate adsorption of the model organic foulants on the silica surface. Adsorption is indicated by changes in the vibration frequency of the piezoelectric quartz-crystal sensor, and the amount of organic molecules adsorbed can be calculated from the frequency change using the Sauerbrey equation [66] (Eq. 6) provided that the adsorbed layer is rigid (i.e., experiences low energy dissipation):

$$\Delta f = \frac{-2f_0^2}{A\sqrt{\rho_q\mu_q}} \Delta m$$

where Δf is change in frequency (Hz), $f_0$ is the resonant frequency (Hz) of the crystal sensor, Δm is change in mass adsorbed (kg), A is the piezoelectrically active crystal area (m²), $\rho_q$ is the density of quartz (kg/m³), and $\mu_q$ is the shear modulus of quartz (Pa).
Experiments using dextran, HA, and sodium alginate showed negligible change in the vibration frequency of the silica-coated crystal sensor, indicating no adsorption of these compounds on the silica surface. This is consistent with the very high negative zeta potentials of humic acid and alginate (Fig. 3-3) and consequently strong electrostatic repulsion between these molecules and the negative silica surface.

Significant adsorption of BSA on silica surface was observed. Fig. 3-2 presents the areal mass of BSA adsorbed as well as the thickness of the adsorbed layer, calculated from the Sauerbrey equation. A comparison of the Sauerbrey model fit to that by a viscoelastic model [64] indicates that a rigid layer is adsorbed and that the Sauerbrey equation is valid. The calculated thickness of the adsorbed layer indicates a monolayer of BSA adsorbed on the surface of the silica coated crystal, suggesting that the presence of BSA may change the surface properties of the silica colloids and hence their interactions with the membrane and other silica colloids.

3.5.3 Impact of the organic foulants on the physicochemical properties of silica colloids.

Adsorption of dissolved organic compounds on the surface of ST-XL may alter its surface properties, e.g., zeta potential and particle size, and consequently impact the interactions among ST-XL colloids. Surface zeta potential and hydrodynamic diameter of ST-XL were measured in the presence and absence of the model organic foulants, and the influence of the model organics under relevant solution conditions is demonstrated in Figs. 3-3 and 3-4.
It is worth noting that although electrophoretic mobility measurement using phase analysis light scattering provides an average zeta potential of all particles in a suspension, the size and concentration (1 or 20 mg/L) of dissolved organic compounds in the mixed suspensions were so small that the free organic molecules in the mixture had negligible impact on the zeta potential of the suspension. Zeta potential measurements of the organic foulants alone at these concentrations yielded non-detectable signals. The zeta potential and size of the organic foulants reported in Table 3-1 were achieved using much higher concentrations: at least 100 mg/L for HA and 1 g/L for dextran, alginate and BSA. Therefore, it is safe to consider that the measured zeta potential or mean particle size of the mixed suspensions represents that of the ST-XL with or without the model organic foulants adsorbed on the surface.

As shown in Fig. 3-3, the zeta potential of the ST-XL was not affected by dextran or HA despite the zeta potentials of both dextran and HA being very different from that of the silica colloids. Meanwhile, no significant changes in particle size were observed in the presence of these two organic compounds (Fig. 3-4), indicating no adsorption of HA dextran on the ST-XL colloidal surface. No significant change in zeta potential of particle size of the ST-XL colloids is again observed in the presence of alginate. This is consistent with the QCM-D measurements that showed no adsorption of these compounds on silica-coated quartz crystal sensors.

In the presence of the model protein BSA, however, the magnitude of the zeta potential of the silica colloids decreased notably and the reduction increased with increasing BSA concentration (Fig. 3-3). In addition, a careful examination of the particle size of ST-XL suggests the presence of an adsorbed BSA layer under these
conditions (Fig. 3-4). In the presence of 20 mg/L of BSA, the diameter of ST-XL increased by approximately 7 nm. The reduced zeta potential and increase particle size are consistent with the adsorption of a monolayer BSA on the silica surface observed in the QCM-D experiments. Data in Figs. 3-3 and 3-4 also indicate that surface coverage of BSA increases with BSA concentration.

3.5.4 Impact of the organic foulants on membrane surface zeta potential.

The zeta potential of the NF 270 membrane in 10mM NaCl solution at pH = 5.0 is -23.6 ± 1.5 mV. Membrane surface zeta potential measurements in the presence of each model foulant were performed immediately after those without organic foulants using the same membrane coupon. Fig. 3-5 illustrates the effect of the four model organic foulants on the membrane surface zeta potential. Changes in membrane surface zeta potential upon exposure to the organic foulants are presented. Negative values indicate reduction in the negative zeta potential, while positive values represent increases.

All model organic foulants except dextran caused notable changes in membrane surface zeta potential, indicating significant adsorption of BSA, alginate and HA on the membrane surface. While adsorption of the highly negatively charged HA and alginate led to an increase in the magnitude of the negative membrane surface zeta potential, BSA significantly reduced its magnitude due to its lower charge density. These changes suggest that HA and alginate will increase the electrostatic repulsion between the membrane and the ST-XL colloids, while BSA will have an opposite effect.
3.5.5 Cross-flow filtration results.

Fouling experiments were performed with feed waters containing ST-XL alone, an organic foulant alone and both the ST-XL and an organic foulant. Concentrations of ST-XL and the organic foulants were 100 mg/L and 20 mg/L, respectively, in all experiments. Fig. 3-6 shows the membrane flux decline results of all four sets of experiments, each with a different model organic foulant.

In order to examine the three proposed combined fouling mechanisms, the combined fouling layer resistance was compared to that predicted from the individual foulant resistance using a resistance in series model. The predicted value, calculated by summing the resistances of the individual colloidal and organic fouling layer, is referred as "the sum" in the discussion hereafter.

The resistance of the fouling layer was calculated using a rearrangement of Darcy's Law (Eq. 1), where the trans-membrane osmotic pressure ($\Delta \pi_m$) was calculated following a previously published method [18, 19]. Rearranging the film-theory equation produces the following expression [18],

$$\Delta \pi_m = f_{oa} (C_m - C_p) = f_{oa} C_b R_o \exp\left(\frac{v}{k}\right)$$

which relates the trans-membrane osmotic pressure to the bulk molar salt concentration ($C_b$), the observed salt rejection ($R_o = 1 - C_p/C_b$), and the mass-transfer coefficient ($k$) through the osmotic coefficient $f_{oa}$ [67]. Since low salt concentrations were used in this study, van't Hoff's equation was used to determine $f_{oa}$ [19].

As the experiments were performed under laminar conditions, the initial mass-transfer coefficient, $k_0$, was calculated during the conditioning phase using Eq. 8,
\[ k_0 = 0.808 \left( \frac{6QD_\infty^2}{WHL} \right)^{1/3} \]  

Here, \( D_\infty \) is the bulk diffusion coefficient of the solute, \( Q \) is the volumetric feed flow rate, \( W \) is the channel width, \( H \) is the channel height, and \( L \) is the channel length. Plugging values of the initial permeate flux \( v_o \), \( k_o \) and the observed salt rejection \( R_o \) during the conditioning stage into the second half of Eq. 7 allows calculation of the intrinsic salt rejection \( R_i \) \( (R_i = 1 - C_p/C_m) \). \( \Delta x_m \) during the fouling experiment was then calculated using the first half of Eq. 7 from the measured \( C_p \) assuming a constant \( R_i \).

Observed salt rejection during colloidal fouling alone decreased slightly from 55.0 to 52.1% (Fig. 3-8), which agrees well with the modeling results of calculated CECP for the NF270 membrane [18, 19]. These results show that silica colloid cake-enhanced concentration polarization has negligible contribution to the flux decline of the NF270 membrane due to its low salt rejection. Therefore, contrary to other studies [20], CECP as a combined fouling mechanism will not be discussed here.

Fig. 3-7 compares the calculated cake/gel layer resistances for each set of fouling experiments. The resistances are plotted as a function of cumulative permeate volume. This normalizes the plots, as the amount of colloidal or organic foulant transported to the membrane surface at a given permeate volume during the combined fouling experiment should be the same as that during colloidal fouling or organic fouling experiment if there are no organic-silica interactions.

The flux decline rates during the initial stage of fouling for all experiments are summarized in Table 3-2. Salt rejections during selected experiments are presented in Fig. 3-8. The effect of each organic foulant is discussed below.
3.5.5.1 Combined fouling with dextran.

Fig. 3-6a compares the membrane flux during filtration of the dextran solution, the ST-XL suspension and the mixture of dextran and ST-XL. The corresponding fouling layer resistances for these experiments are plotted in Fig. 3-7a.

Dextran alone did not foul the membrane, as evidenced by the stable membrane flux throughout the organic fouling experiment. The ST-XL colloids caused significant decline of the membrane flux. Up until the latter stages of fouling, combined fouling with dextran creates a similar fouling layer resistance as that with silica alone. Towards the end of the experiment, however, the combined cake layer resistance begins to rapidly increase compared to the sum term, indicating a synergistic effect. Since dextran does not adsorb on ST-XL, the observed synergy indicates that both hindered back diffusion and a change in cake layer structure are present. Because this change in resistance is seen in the latter stages of fouling after significant accumulation of foulants has occurred, it is likely that the increase in resistance is caused by a change in cake layer structure as dextran fills in the interstitial pore space of the cake layer and that hindered back diffusion remains a small but contributive effect during combined fouling with dextran.

3.5.5.2 Combined fouling with HA.

As shown in Fig. 3-6b, fouling by HA alone caused only slight flux decline. The combined fouling experiment with HA and ST-XL showed no synergistic effect in the beginning stage. In fact, a closer look at the initial flux decline rates (Table 3-2) during filtration of the ST-XL suspension and the mixture of HA and ST-XL (0.77 and 0.39 L⁻¹, respectively) shows that the presence of HA reduced the initial flux decline rate. This is attributed to HA adsorption onto the membrane surface, which increases the electrostatic
repulsion between the foulants and the membrane. In the latter fouling stages, however, the membrane flux during combined fouling deviated from the calculated sum and showed a synergistic effect that continued to increase with filtration time. As HA does not adsorb to ST-XL, this increase is either due to the hindered back diffusion effect or to the increased resistance caused by a mixed fouling layer with HA interspersed in the ST-XL cake layer.

3.5.5.3 Combined fouling with sodium alginate.

Initial flux decline in the presence of sodium alginate alone was the most substantial of all the organic foulants (Fig. 3-6c). The alginate fouling layer also displayed active salt rejecting characteristics, as evidenced by the steady increase in observed salt rejection over the length of the experiment (Fig. 3-8). Strong synergism was observed during the filtration of the ST-XL-alginate mixture (Fig. 3-7c). The fouling layer resistance calculated during combined fouling is significantly higher than the calculated sum of individual fouling layers in spite of the slightly reduced initial fouling rate (Table 3-2, 0.77 vs. 0.44 L\(^{-1}\)) caused by the increased repulsion between ST-XL and the membrane. Salt rejection during the combined fouling experiment remained stable over time, indicating either the impact of CECP and salt rejection by the fouling layer were negligible, or the two effects cancelled each other out. The same combined fouling mechanisms for HA (hindered back diffusion and cake layer structure) are expected to apply to alginate. However, the synergistic effect caused by sodium alginate is greater in the initial stages of filtration compared to that by HA. It is postulated that this is due to a more significant effect of the hindered back diffusion mechanism. Since sodium alginate solution is much more viscous than the other model foulants, the back diffusion of the
ST-XL colloids in the CP layer may be more severely hindered, causing faster accumulation of ST-XL and therefore a greater flux decline rate.

3.5.5.4 Combined fouling with BSA.

Flux decline in the presence of BSA alone appears to be caused by a compressible fouling layer that increases in resistance over time (Fig. 3-6d). The mixture of BSA and ST-XL caused much greater flux decline than the sum of the contribution from each foulant (Fig. 3-7d). The greater initial flux decline rate can be explained by the faster deposition of ST-XL due to the reduced electrostatic repulsion between ST-XL and the membrane as well as that between ST-XL colloids, a result of the lower negative surface zeta potential upon adsorption of BSA (Fig. 3-3 and 3-5). Analysis of the feed water showed an increase, instead of the expected decrease, in turbidity with filtration time, resulting from the formation of ST-XL aggregates (Fig. 3-9). Storage of the same feed solution over time did not show similar increase in particle size, indicating that these aggregates likely formed in the CP or fouling layer. This observation suggests that the cake layer formed was dynamic and some ST-XL aggregates were washed off from the membrane surface during cross-flow filtration. This is consistent with the large fluctuation of salt rejection observed during the combined fouling experiment (Fig. 3.8). While it is unclear if the decrease in salt rejection is due to CECP or a disturbance in the fouling layer, calculations show that the increase in trans-membrane osmotic pressure over the course of the experiment has a negligible contribution to flux decline.

The synergism during the combined fouling experiment continued throughout the experiment. Because BSA adsorbs on silica surfaces, the observed synergism results from the interplay of all the three combined fouling mechanisms discussed in the Theory. In
addition, the observed aggregation of foulants in the cake layer as well as the change in the growth rate of the combined fouling layer resistance at permeate volume of about 2.5 L (Fig. 3-7d) suggests a shift in the combined fouling layer structure towards the latter stages of filtration. These results with BSA show that the effects of organic foulant adsorption on silica surface are complex and can have important implications on membrane flux decline.

3.6 Conclusions

The flux decline behavior of a nanofiltration membrane in the presence of four model organic macromolecules and one model silica colloidal foulant was investigated to examine mechanisms responsible for the synergism observed in combined fouling. All model organic foulants tested exhibited a synergistic effect when in combination with the model silica colloids. The extent of the synergy, however, strongly depends on the molecular characteristics of the organic foulant. The three hypothesized mechanisms: increased resistance of the mixed fouling layer, hindered back diffusion, and organic foulant adsorption were shown to have varying effects on combined fouling, depending on the specific organic foulant. The greatest synergism was observed in the presence of an interacting organic foulant, BSA, which can adsorb on silica colloids as well as the membrane surface to reduce repulsive interaction between foulants and the membrane as well as that among foulants. Adsorption of the organic foulant to the clean membrane surface only impacts the very beginning fouling stage and does not have a lasting effect on the overall flux decline behavior. The study also showed that the interplay of the various mechanisms in combined fouling can be very complex, calling for further investigation of the combined fouling process. More comprehensive models that
incorporate the combined fouling mechanisms suggested here are needed to properly predict the fouling of complex solutions.

Acknowledgements

We thank the National Science Foundation (Award CTS-0552413) for funding this study. We also thank Candace Marbury and Andrew Kuehler for their assistance in collecting some of the experimental data.
Table 3-1 Characteristics of model foulants *

<table>
<thead>
<tr>
<th>Model Foulant</th>
<th>Zeta Potential (mV)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dextran</td>
<td>-7.2 ± 1.5</td>
<td>4.3 ± 0.2</td>
</tr>
<tr>
<td>BSA</td>
<td>-20.7 ± 0.9</td>
<td>6.9 ± 0.2</td>
</tr>
<tr>
<td>Humic Acid</td>
<td>-37.9 ± 1.2</td>
<td>n/a</td>
</tr>
<tr>
<td>Sodium Alginate</td>
<td>-45.0 ± 1.2</td>
<td>5.12 ± 2.2</td>
</tr>
<tr>
<td>Silica (ST-XL)</td>
<td>-37.9 ± 0.4</td>
<td>60.7 ± 1.2</td>
</tr>
</tbody>
</table>

* Reported values are the average of 5 measurements with standard deviation. The solution condition used was 10 mM NaCl and pH 6.0 ± 0.2.

Table 3-2 Initial flux decline rates of all fouling experiments. The initial flux decline rate is calculated by fitting data collected during the first 100 min. by a linear function assuming \( J/J_0 = 1 \)

<table>
<thead>
<tr>
<th>Foulant(s)</th>
<th>Initial Flux Decline Rate (L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-XL</td>
<td>0.77</td>
</tr>
<tr>
<td>Dextran</td>
<td>0.02</td>
</tr>
<tr>
<td>Dextran + ST-XL</td>
<td>0.81</td>
</tr>
<tr>
<td>Humic acid</td>
<td>0.04</td>
</tr>
<tr>
<td>Humic acid + ST-XL</td>
<td>0.39</td>
</tr>
<tr>
<td>Sodium alginate</td>
<td>0.25</td>
</tr>
<tr>
<td>Alginate + ST-XL</td>
<td>0.44</td>
</tr>
<tr>
<td>BSA</td>
<td>0.16</td>
</tr>
<tr>
<td>BSA + ST-XL</td>
<td>1.07</td>
</tr>
</tbody>
</table>
Figure 3-1 Schematic description of the cake/gel and CP layers of colloids and macromolecules after cake/gel layer formation. $C_c$: concentration at the membrane surface; $C_m$: bulk concentration; $D$: back diffusion coefficient. Subscript: $c$ = colloids, $m$ = macromolecules. The color gradient correlates to the concentration gradient present at the membrane surface as a result of concentration polarization.

Figure 3-2 Areal mass and thickness of the adsorbed BSA layer on the silica surface. Phase 1: 10 mM NaCl; Phase 2: 20 mg/L BSA in 10 mM NaCl; Phase 3: 10 mM NaCl.
Figure 3-3 Surface zeta potential of ST-XL in the presence of varying concentrations of model organic foulants. Horizontal black line with striped halo represents the average and standard deviation of ST-XL surface zeta potential in the absence of model organic foulants. All test solutions contained 10 mM NaCl and the pH was 6.0 ± 0.2. Data over the pH range 4 - 10 is available in Appendix III.

Figure 3-4 Particle size of ST-XL in the presence of varying concentrations of model organic foulants. Black line with striped halo represents the average and standard deviation of the measured particle size of ST-XL in the absence of model organic foulants. All test solutions contained 10 mM NaCl, and the pH was 6.0 ± 0.2. Data over the pH range 4 - 10 is available in Appendix III.
Figure 3-5 Effect of organic foulants on membrane surface zeta potential (10mM NaCl, pH = 5.0 ± 0.5). Values represent the change from the original membrane zeta potential of -23.6 ± 1.5 mV.)
Figure 3-6 Normalized flux of the individual organic and colloidal fouling and the combined fouling experiments for, a) dextran; b) humic acid; c) sodium alginate; and d) BSA. (Entire experiments available in Appendix I)
Figure 3-7 Calculated cake/gel layer resistances ($R_c$) of each fouling experiment compared to the sum of individual foulant contribution for a) dextran; b) humic acid; c) sodium alginate; and d) BSA. (Entire experiments available in Appendix I)
Figure 3-8 Salt rejections observed during selected filtration experiments. (Complete experimental data available in Appendix II).

Figure 3-9 Feed solution turbidity measurements of selected filtration experiments.
4. Fundamental Mechanisms of Three-Component Combined Fouling with Experimental Verification

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4.1 Abstract

A novel fundamental theory is developed to investigate combined fouling due to colloids (STXL), macromolecules (bovine serum albumin, alginate, and dextran), and solute ions (NaCl). This theory unifies singlet, doublet, and triplet fouling phenomena, including cake-enhanced osmotic pressure and binary colloidal fouling models, and provides the flux equation for three component combined fouling, defined as a combined flux. The strong form of the equivalent flux refers to the additive flux due to a linear superposition of individual fouling, and the weak form proposed in this study indicates the permeate flux resulting from a conceptual phenomenon that colloidal and macromolecular deposit layers are vertically stratified on the membrane surface. Structural compression of the BSA-gel layer is suggested by the current theory while alginate- and dextran-gel layers appear to provide constant specific cake resistance. The equivalent flux (of the weak form) and combined fluxes, predicted using the current theory, provide the upper and lower bounds of the measured flux of the combined fouling, while the additive flux (i.e., the strong form) intersects and/or underestimates the combined flux.

Keywords – Colloidal fouling, NOM fouling, Organic fouling, Combined fouling, Equivalent flux, Dead-end Filtration

2 Submitted to Langmuir on Nov. 7th, 2008
4.2 Introduction

With ever increasing global demands for food, energy, and water (FEW) in the 21st century [68], energy requirements to produce safe drinking water are already of great concern in conjunction with water quality and scarcity [69, 70]. Currently, economic development of membrane processes results in clean water production from non-traditional sources, i.e. brackish water and wastewater. As one of the pressure-driven membrane filtration processes, nanofiltration (NF) receives close attention due to its capability to remove multi-valent ions and dissolved organic matters using significantly less pressure than that required for reverse osmosis. Similar to other liquid separation membrane processes, NF is subject to fouling due to colloids, organic/inorganic components, and microorganisms, which inherently reduce the membrane performance and increase the ratio of operation and maintenance cost to water production rate. Pretreatment of NF using microfiltration (MF) or ultrafiltration (UF) often provides incomplete rejection of fine particulate materials such as sub-micron colloids and dissolved organic matter. Formation of a colloidal cake and/or organic gel layer on NF membrane surfaces seriously hampers the filtration efficacy and requires frequent cleaning. In this light, several protocols for fouling prevention or minimization have been suggested, such as using low fouling membrane materials [29, 41-43], improving pretreatment of the feed stream [44-47], optimizing system configurations [18, 33], and using hybridized systems [71-73]. An integrated understanding of responsible fouling mechanisms is, however, still in great demand for developing and applying control strategies for fouling mitigation.
Due to the physical, chemical, and biological complexity of feed water collected from natural and engineered sources, fouling phenomena occurring with one or two types of foulants are extremely rare cases in purification systems. Significance of interactions between foulant species has been recognized in several systematic studies [36, 37, 48], indicating that fouling analyses of individual foulants cannot be easily extrapolated to explain complex, multi-foulant filtration tendencies. In-depth understanding of the behavior of individual foulants does not always provide good quantitative insight to cases where two or three foulants co-exist in the feed stream. Simple superposition of individual foulant behaviors fails to depict the synergistic fouling trend when multiple foulants are combined. Two-component fouling occurs in colloidal cake formation of mono-dispersed particles in reverse osmosis (RO) processes [18-20, 35, 74-77] and deposition of bi-dispersed particulate suspensions in crossflow processes [78, 79]. Introduction to the diffusive tortuosity concept [80-82] and theoretical development of the cake-enhanced osmotic pressure (CEOP) [18, 75] successfully analyzed the effects of colloidal cake formation on the performance of RO filtration. Although the theory of cake-enhanced concentration polarization (CECP) [19] adequately explains the hindered diffusion of salts within the colloidal cake layer and its influence on permeate flux decline, both CEOP and CECP are fundamentally limited to fouling propensity caused by two types of foulants, i.e., colloids and solute ions. Co-existence of dissolved organic matters and poly- [38] or bi-dispersed colloidal particles in the brackish feed stream fundamentally restricts employing the CEOP/CECP concept for quantitative analysis of flux decline behavior. Most filtration processes in real practice involve feed water
consisting of at least three foulants such as colloidal particles, organic matter, and salt ions.

When colloids and organics are both present in brackish or saline feed water, the aggravated flux decline by the three foulants (i.e., particles, organics, and salt ions) was ascribed to "combined fouling" [20, 35], which was not easily characterized using known information from individual fouling propensities. Dichotomous phenomena have been found in combined fouling studies depending on the salt rejection of the membrane. Using a NF membrane of high rejection (84.5–86.4%), Lee et al. [20] observed that the combined fouling of silica colloids and natural organic matter (NOM) caused lower permeate flux than each individual flux in the presence of salt ions. However, the permeate flux of combined fouling was higher (in the later stage of filtration) than that of the equivalent flux inferred from superposition of the individual contributions of colloidal and organic fouling. The combined fouling layer seemed to perform as a 'active membrane' formed by the accumulation of organic materials above the membrane surface, providing higher salt rejection ratio than those of individual fouling cases. On the other hand, Li and Elimelech [35] used a low salt rejection (44.0%) NF membrane and observed that the combined fouling (of silica colloids and Suwannee River humic acid (SRHA)) was more severe than the linear superposition of the two foulants in terms of the additive flux (see section 4.3.4.1 for details.). The enhanced osmotic pressure (of salt ions) did not seem to be an important factor when using NF membranes with salt low rejection. In Li and Elimelech's work [35], the measured salt rejection did not significantly vary with the three different types of fouling experiments, i.e., colloids-alone, organics-alone, and colloids and organics combined. In general, the degree of
combined fouling seems to be not only dependent on the salt rejection but also on the foulant-foulant (specifically, colloid-organic) interactions.

In spite of the crucial need of analytic tools for combined fouling, the current literature seriously lacks mechanistic models that can fundamentally characterize fouling mechanisms and predict the filtration performance. The goal of this study is, therefore, to develop an integrated model for combined fouling due to three different foulants, which specifically unifies two-component fouling models such as CEOP/CECP and bi-dispersed colloidal fouling in addition to the single-component fouling scenarios.

4.3 Theory

Fouling behaviors with one, two, and three foulants, named in this study as singlet, doublet, and triplet fouling phenomena, are fundamentally analyzed using Darcy’s law with responsible mechanisms.

4.3.1 Singlet fouling.

4.3.1.1 Colloids alone.

Darcy’s law describes the filtration flux with the colloidal cake formation [75, 83-87] as shown in Fig. 4-1(a):

\[ v_w = \frac{\Delta P}{\mu(R_m + R_c)} \]  

(1)

where \( v_w \) is the permeate flux, \( \Delta P \) is the applied pressure, \( \mu \) is the solvent viscosity, and \( R_m \) is the membrane resistance. Eq. (1) assumes that the osmotic pressure of colloidal particles is negligible in comparison to the influence of cake resistance. Considering a
uniform distribution of colloids within the cake layer, the cake resistance $R_c$ is expressed as,

$$R_c = \hat{R}_c (\phi_c) \delta_c$$

(2)

where $\hat{R}_c$ is the specific cake resistance (i.e., the inverse permeability), $\delta_c$ is the thickness of the colloidal cake layer, and $\phi_c$ is the cake volume fraction.

### 4.3.1.2 Organic matter alone.

When organic macromolecules form a gel layer [88-92] as shown in Fig. 4-1(b), one can replace the subscript $c$ of Eqs. (1) and (2) with $g$ for ‘gel’:

$$\nu_w = \frac{\Delta P}{\mu (R_m + R_g)}$$

(3)

and

$$R_g = \hat{R}_g (\phi_g) \delta_g$$

(4)

The macromolecular gel resistance $R_g$ (as a function of the gel concentration, $\phi_g$) is the product of the specific resistance, $\hat{R}_g$, and the gel thickness, $\delta_g$. The osmotic pressure of macromolecules is also neglected in Eq. (3) in the presence of the gel layer.

### 4.3.1.3 Solute ions alone.

The osmotic pressure of solute ions retained on the membrane surface contributes to the permeate flux decline [93-95]:

---

$^3$ In this study, $\phi$ is used for the concentration (volume fraction) of macromolecules, which is different from the colloidal concentration $\phi$. 
\[ \nu_w = \frac{\Delta P - \Delta \pi_m}{\mu R_m} \]  \hspace{1cm} (5)

where \( \Delta \pi_m \) is the osmotic pressure difference between the membrane surface and permeate flow. van’t Hoff’s equation is often used to calculate osmotic pressure:

\[ \Delta \pi_m = R_g T (C_m - C_p) \]  \hspace{1cm} (6)

where \( R_g \) is the universal gas constant, \( T \) is the absolute temperature, and \( C_m \) and \( C_p \) are solute molarities on the membrane surface and in the permeate stream, respectively.

The transport equation of solute ions in the viscosity of the membrane surface is

\[ D_0 \frac{\partial C}{\partial y} + \nu_w C = \nu_w C_p \quad \text{for} \quad 0 \leq y \leq \delta_s \]  \hspace{1cm} (7)

where \( D_0 \) is the solute diffusivity in free space (i.e., within the bulk solvent), and \( C \) is the solute molarity in the CP layer of the thickness \( \delta_s \) above the membrane surface (i.e., \( y = 0 \)). The transverse profile of \( C \) above the membrane surface is shown in Fig. 4-1(c).

**4.3.2 Doublet fouling.**

**4.3.2.1 Colloids and solute ions.**

The flux equation for the doublet fouling by colloids and solute ions [18, 19, 75, 87] can be written as

\[ \nu_w = \frac{\Delta P - \Delta \pi_{m,c}}{\mu (R_m + R_c)} \]  \hspace{1cm} (8)

which combines Eqs.(1) and (5) to incorporate colloidal cake formation and hindered diffusion of solutes within the colloidal cake. \( \Delta \pi_{m,c} \) is the osmotic pressure difference in the presence of the colloidal layer between the membrane-cake interface and permeate.
stream, which is generally greater than $\Delta\pi_m$ of Eq. (5). The transport equation for solutes has a similar form to Eq. (7):

$$D'\frac{\partial C}{\partial y} + v_w C = v_w C_p$$

(9)

except a hindered diffusivity $D'$ within the deposit layer. Assuming the CP layer thickness of solute ions is greater than or equal to that of the colloidal cake layer, i.e., $\delta_c \leq \delta_s$, one can write

$$D' = \begin{cases} D_c (= D_0 \frac{1 - \phi_c}{\tau_c}) & \text{for } 0 < y < \delta_c \\ D_0 & \text{for } \delta_c < y < \delta_s \end{cases}$$

(10)

where $\tau_c$ is the diffusive tortuosity of the cake layer, which accounts for the hindered diffusion of solute ions through the void space of the colloidal cake layer. (See section 4.3.3.3 for details.) Integration of Eq. (9) from the membrane surface ($y = 0$) to the top of the solute CP layer ($y = \delta_s$) yields

$$v_w = \left[ \frac{\delta_c + \delta_s - \delta_c}{D_c} \right]^{-1} \ln \frac{C_m - C_p}{C_f - C_p} = k'_f \ln \frac{\Delta C_m}{\Delta C_f}$$

(11)

where

$$\Delta C_m = C_m - C_p$$

(12)

$$\Delta C_f = C_f - C_p$$

(13)

$$k'_f = \frac{D_0}{\delta_s}$$

(14)

and

$$\delta_s = \left( \frac{\tau_c}{\phi_c} \right) \delta_c + (\delta_s - \delta_c) > \delta_s$$

(15)
Here, $k'_f$ of Eq. (14) represents the effective mass transfer coefficient [96] of solutes, which are taking tortuous paths generated in the interstitial spaces of the colloidal cake layer and performing random walk-like movements [82] above the cake surface along the length, $\delta_l - \delta_c$. It is assumed that the concentration polarization of colloidal particles above the cake surface does not significantly hinder the solute back-diffusion. In the absence of the colloidal cake layer, the following convergences are considered: $\phi_c \rightarrow 0^+$, $\tau_c \rightarrow 1^+$, and $\delta'_s \rightarrow \delta'^+$.\[s\]

Effects of the colloidal cake on the permeate flux due to hindered diffusion of solute ions can be understood using two ideal, exemplary cases, shown in Fig. 4-2. First, if the presence of the colloidal cake layer does not change the solute concentration on the membrane surface, $C_m$, then the effective thickness of solute CP layer $\delta'_s$ of Eq. (15) is greater than $\delta_s$ by as much as $(\tau_c/\varepsilon_c - 1)\delta_c$, as shown in Fig. 4-2(a), and $k'_f$ is smaller than $k_f (= D_0/\delta_s)$. In this scenario, Eq. (11) indicates that the permeate flux decreases due to reduced mass transfer coefficient, $k'_f (< k_f)$. Second, if the effective thickness is assumed to be equal to $\delta_l$, then the hindered diffusion enhances the solute concentration on the membrane surface, denoted as $C'_m (> C_m)$ in Fig. 4-2(b). The $C'_m$ higher than $C_m$ generates a larger osmotic pressure difference and therefore lowers the permeate flux as implied in Eq. (8). Both cases clearly indicate the additional flux decline due to the presence of the colloidal cake layer. In reality, the flux decline due to the cake-enhanced osmotic pressure resides between the two ideal cases. Therefore, flux equations from the osmotic pressure model of Eq. (8) and the film theory model of Eq. (11) need to be
coupled using the van’t Hoff equation of Eq. (67) to fully address the convoluted phenomena.

4.3.2.2 Macromolecules and solutes alone.

The doublet fouling of macromolecules and solutes, such as protein fouling in reverse osmosis can be phenomenologically treated like that for colloids and solutes. Ion interactions with macromolecules, generally different from that with colloids, can be treated using the gel layer resistance $R_g(\phi_g)$ in a same way represented in section 4.3.2.1. The flux equation in this case is written as:

$$v_w = \frac{\Delta P - \Delta \pi_{m,g}}{\mu(R_m + R_g)}$$

where $\Delta \pi_{m,g}$ indicates the osmotic pressure difference in the presence of the gel layer.

4.3.2.3 Colloids and macromolecules: A binary suspension.

A feed solution containing colloids and macromolecules can be considered as a binary particle suspension [78, 79, 97]. Darcy’s law for this system is written as

$$v_w = \frac{\Delta P}{\mu(R_m + R_{cg})}$$

where $R_{cg}$ is the hydraulic resistance of a combined layer consisting of colloids and macromolecules:

$$R_{cg} = \hat{R}_{cg}(\phi_c, \phi_g) \delta_{cg}$$

Note that $\phi_g$ represents the volume fraction of macromolecules, i.e., the total volume of macromolecules divided by the interstitial void volume in the colloidal cake layer.
Drag forces exerted on various spherical objects such as an isolated solid sphere, uniformly porous sphere, composite sphere (i.e., a solid core with a permeable shell), and fractal aggregate formed in the diffusion-limited-cluster-aggregation (DLCA) regime, were analytically solved by Stokes [98], Brinkman [99], Masliyah et al. [100], and Kim and Rong [101], respectively. Hydraulic permeabilities (i.e., inverse specific resistance) of swarms of the spherical objects described above were studied using the sphere-in-cell model by Happel [17], Neale el al.[102], and Kim and Rong [103, 104]. Kim and Rong [103] (2005) modeled a fractal aggregate as a composite sphere and calculated the specific resistance of an aggregate cake layer formed on the membrane surface. The tangential-stress-free cell encompasses concentrically the composite sphere, and the void space within the cell determines the mean distance between nearest aggregates. By equating radii of the cell and composite sphere in the previous model [103], we now mimic the combined fouling layer (i.e., colloidal cake layer of which interstitial void spaces are filled with macromolecules) as a swarm of composite spheres, on the surface (at \( r = b \), as shown in Fig. 4-3) of which, the tangential stress is zero.

Using the concentric spherical cell shown in Fig. 4-3, \( \phi_c \) and \( \varphi_g \) can be calculated as

\[
\phi_c = \frac{a_p^3}{b^3}
\]

(19a)

\[
\varphi_g = \frac{n_m a_m^3}{b^3 - a_p^3}
\]

(19b)

where \( n_m \) is the number of macromolecules per colloid in the combined layer of thickness \( \delta_{cg} \). Then, the specific resistance of the combined layer is written as
\[
\hat{R}_{\alpha}(\phi_c, \varphi_g) = \frac{9\Omega_{K_Y}(\alpha, \beta)}{2b^2}
\]  

(20)

where \( \alpha = a_p/\sqrt{\kappa_g} \), \( \beta = b/\sqrt{\kappa_g} \) and \( \kappa_g \) is the permeability of the gel layer represented as

\[
\kappa_g(\varphi_g) = \frac{2a_n^2}{9\varphi_g\Omega_H(\varphi_g)}
\]

(21)

and \( \Omega_H \) is Happel's correction factor [17]:

\[
\Omega_H(\phi) = \frac{6 + 4\phi^{5/3}}{6 - 9\phi^{1/3} + 9\phi^{5/3} - 6\phi^2}
\]

(22)

The expression \( \Omega_{K_Y} \) is calculated using the previous works as a special case stated above:

\[
\Omega_{K_Y}(\alpha, \beta) = \frac{A(\alpha, \beta)\sinh(\Delta) + B(\alpha, \beta)\cosh(\Delta) + 24\alpha\beta^3}{E(\alpha, \beta)\sinh(\Delta) + F(\alpha, \beta)\cosh(\Delta) - 108\alpha\beta}
\]

(23)

where

\[
A(\alpha, \beta) = (18 + 3\beta^2)\alpha^3 - 3\beta(18 + \beta^2)\alpha^2 + (54 + 9\beta^2)\alpha + 6\beta^3(2 + \beta^2)
\]

(24a)

\[
B(\alpha, \beta) = -\beta(18 + \beta^2)\alpha^3 + (54 + 9\beta^2)\alpha^2 - 3\beta(18 + \beta^2)\alpha - 2\beta^4(6 + \beta^2)
\]

(24b)

\[
E(\alpha, \beta) = 27\alpha^3 - 27\alpha^2\beta + 81\alpha - 27\beta(2 + \beta^2)
\]

(24c)

\[
F(\alpha, \beta) = -9\alpha^3\beta + 81\alpha^2 - 27\alpha\beta + 9\beta^2(6 + \beta^2)
\]

(24d)

and

\[
\Delta = \beta - \alpha
\]

(25)
4.3.3 Triplet fouling.

4.3.3.1 Individual aspects of three-foulant transport.

In the feed solution to be filtered using NF/RO membranes, three foultants (such as colloids, macromolecules, and solutes) potentially contribute to at least individual or most likely combined fouling phenomena. Every foulant undergoes collective transport, while being influenced by the other two components. Effective transport of each foulant can be described as follows:

• *Particle transport influenced by macromolecules and solutes*

1. Cake volume fraction $\phi_c$: Solute (assumed to be monovalent and inert) control inter-particle interactions by changing the Debye screening length of the electrostatic double layer repulsion, as described in the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [105, 106]. We assumed that this effect can be phenomenologically described using cake volume fraction as $\phi_c$, a modeling parameter.

2. Effective viscosity: Presence of macromolecules can affect colloidal transport above the membrane surface. Since the number of macromolecules is much larger than that of colloidal particles (i.e., $n_m \gg 1$), we assume that the presence of macromolecules contributes to the effective viscosity that moving colloids experience and hence influences the cake volume fraction $\phi_c$ on the membrane surface.
• Macromolecule transport influenced by solutes and colloids

1. Gel volume fraction $\varphi_g$: The presence of the solute ions can change interactions between macromolecules and influence the local gel structures formed within void spaces of accumulated colloids. The number of macromolecules in the interstitial spaces is controlled by macromolecular interactions to the colloidal swarm forming the combined deposit layer.

2. Hindered Diffusion: When macromolecules exist in the interstitial spaces of the colloidal cake layer, colloidal particles play the role of geometrical obstacles to diffusing macromolecules. As such, the macromolecules undergo hindered transport through tortuous paths within the colloidal swarm. The gel volume fraction, $\varphi_g$, implicitly encompasses effects of macromolecule-macromolecule and macromolecule-colloid interactions.

• Ion transport influenced by macromolecules and colloids

1. Self-influencing diffusive transport: Solute ions influence mutual interactions between three different pairs, i.e., macromolecule-macromolecule, colloid-colloid, and colloid-macromolecule. These ions control the porosity and structure of the colloidal cake and macromolecular gel layers, within which ions undergo collective transport. The combined layer plays a synergetic role of geometrical obstacles in ion back-diffusion, leading to remarkable flux decline due to the enhanced osmotic pressure.
2. Double diffusive tortuosity $\tau_{\text{eq}}$: The diffusive transport of solute ions within the combined layer is hindered by tortuous structures of two different scales. While the interstitial voids among colloids are filled with small macromolecules, solute Brownian motion is hampered by (a) microscopic tortuous paths formed within local macromolecule swarms and (b) macroscopic convoluted routes generated among colloidal particles. The mean free path of solute ions is assumed to be much smaller than sizes of colloids and macromolecules so that Knudsen diffusion [107] is excluded in the ion transport. The coupled hindrance of solute diffusion in the combined gel-cake layer is a key factor in investigating the triplet fouling phenomena to be modeled using $\phi_c$ and $\phi_k$. See section 4.2.3.3 for details.

4.3.3.2 Governing equations.

In the case of the triplet fouling, the permeate flux is governed by solute transport through the combined layer, represented by combining Eqs. (8) and (17):

$$v_w = \frac{\Delta P - \Delta \pi_{\text{m.cg}}}{\mu(R_m + R_{cg})}$$  \hspace{1cm} (26)

The solute transport can be written as

$$D \frac{\partial C}{\partial y} + v_w C = v_w C_p$$  \hspace{1cm} (27)
where

\[
D^* = \begin{cases} 
D_{cg} = D_0 \frac{1 - \phi_c}{\tau_c} \frac{1 - \phi_g}{\tau_g} & \text{if } 0 < y < \delta_{cg} \\
D_0 & \text{if } \delta_{cg} < y < \delta_s
\end{cases}
\]  

(28)

whose meaning is described in Fig. 4-4. Integration of Eq. (27) from the membrane surface to the top of the solute CP layer yields

\[
v_w = \left[ \frac{\delta_{cg} + \delta_s - \delta_{cg}}{D_{cg}} \right]^{-1} \ln \frac{C_m - C_p}{C_f - C_p} = k_f^* \ln \frac{\Delta C_m}{\Delta C_f}
\]  

(29)

where

\[
k_f^* = \frac{D_0}{\delta_s^*}
\]  

(30)

and

\[
\delta_s^* = \left( \frac{\tau_g \tau_c}{\varepsilon_g \varepsilon_c} \right) \delta_{cg} + (\delta_s - \delta_{cg}) > \delta_s
\]  

(31)

Substitution of Eq. (29) into (26) gives

\[
v_w = \frac{\Delta P - \Delta \pi_f \exp \left( v_w / k_f^* \right)}{\mu \left[ R_m + \tilde{R}_{cg} (\phi_c, \phi_g) \delta_{cg} \right]}
\]  

(32)

where \( \Delta \pi_f \) is the osmotic pressure difference between feed stream and permeate

\[
\Delta \pi_f = R_{ob} R_g T C_f = R_{ob} \pi_f
\]  

(33)

where \( \pi_f \) is the absolute osmotic pressure of the feed, i.e.,

\[
\pi_f = R_g T C_f
\]  

(34)

and \( R_{ob} \) is the observed rejection defined as

\[
R_{ob} = 1 - \frac{C_p}{C_f}
\]  

(35)
4.3.3.3 Diffusive tortuosity.

How the structure of the porous medium affects the tracer diffusion has been a century-long scientific question. Maxwell [108] developed the tortuosity expression as a function of the volume fraction $\phi$ of the porous medium through which inert solutes are transported under the influence of an electric field, i.e.,

$$\tau = 1 + \frac{1}{2}\phi$$

(36)

and an empirical correlation [80, 81] by fitting a plethora of experimental results was developed:

$$\tau = 1 - \ln \varepsilon^2$$

(37)

where $\varepsilon = 1 - \phi$. Employing the diffusive tortuosity [82] into filtration theory successfully explained the flux decline behavior due to CEOP and CECP.

In this study, the fundamental expression from Maxwell's electromagnetic theory is used for the analysis of the triplet fouling phenomena. Here, we compare the hindered diffusivity within the combined layer (of Eq. (28)) to that in the colloidal cake layer (of Eq. (10)) using Maxwell's equation. Assuming $\phi_c$ and $\phi_g$ are small enough, the weight factor of $\delta_{cg}$ in the first term of Eq. (31) can be approximated, neglecting coupled terms, as

$$\frac{\tau_g \tau_c}{\varepsilon_g \varepsilon_c} = \frac{1 + \frac{1}{2}\phi_c + \frac{1}{2}\phi_g}{1 - \phi_c - \phi_g} = \frac{1 + \frac{1}{2}(\phi_c + \phi_g)}{1 - (\phi_c + \phi_g)} \approx \frac{\tau_{cg}}{\varepsilon_{cg}}$$

(38)

where $\varepsilon_{cg}$ (= $1 - \phi_c - \phi_g$) is the porosity of the combined layer composed of colloids and macromolecules, and $\tau_{cg}$ (= $1 + (\phi_c + \phi_g)/2$) is the combined diffusive tortuosity. The linear analysis of Eq. (38) may deviate from the true depiction of complex hindered
diffusion within a closely-packed combined layer, but it explains the combined effects of macromolecules, existing in interstitial voids of packed colloids, on solute back-diffusion.

4.3.3.4 Dead-end filtration modeling.

Modeling the transient dead-end filtration phenomena gives a good fundamental insight to the initial stage of crossflow filtration [74, 109]. To investigate the performance of dead-end filtration with three foulants, the following assumptions are made:

1. The CP layers of colloids, macromolecules, and solutes forms almost instantaneously in the beginning of the filtration; the influence of colloidal and macromolecular CP layers on the permeate flux is negligible, especially once the combined layers are formed.
2. Colloids are assumed to be uniformly distributed in the combined layer, and so are macromolecules in the voids among packed colloids.
3. Growth of colloidal cake and macromolecular gel layers is the slowest processes that govern the rate of the permeate flux decline. During dead-end filtration, the solute ions are assumed to reside in a (quasi or dynamic) equilibrium state; the transient variation of the ion concentration, $\frac{\partial C}{\partial t}$, is negligible.

Using the assumptions above, we describe the mass transport from the bulk phase to the membrane surface as follows, considering only the transient increase in the thickness of the combined cake layer, $\delta_{cg}$:

$$
[\phi_c + \varphi_g -(\phi_f + \varphi_f)] \frac{d\delta_{cg}}{dt} = (\phi_f + \varphi_f) \nu_w
$$

(39)
Substitution of Eq. (39) into (32) gives the transient expression of $\delta_{cg}$ as a function of time

$$\delta_c(t) = \delta_{cg,0} \left( \sqrt{1 + w_{cg} t} - 1 \right)$$

(40)

where

$$w_{cg} = \frac{2 v_{w0}}{\Psi_{cg} \delta_{cg,0}}$$

(41)

$$\Psi_{cg} = \frac{\phi_c + \phi_g - (\phi_f + \phi_f)}{\phi_f + \phi_f}$$

(42)

$$v_{w0} = \frac{\Delta P - \Delta \pi_f}{\mu R_m}$$

(43)

and

$$\delta_{cg,0} = \frac{R_m}{\tilde{R}_{cg}(\phi_c, \phi_g) + \Delta \pi_f / \mu \Delta_D_{cg}}$$

(44)

Note that $w_{cg}$ has a dimension of inverse time, and $\delta_{cg,0}$ represents the characteristic thickness of the combined cake layer.

The derivation of Eq. (40), first, presumes

$$\delta_s - \delta_{cg} \ll \delta_{cg}$$

(45)

from Eq. (31) implying $\delta_s = \delta_{cg}$, which provides

$$k_f^* \equiv \frac{D_{cg}}{\delta_{cg}}$$

(46)

second, assumes $J(= v_w / k_f^*) < 1$, which is equivalent to $\Delta C_m / \Delta C_f < e^1 = 2.72$, and, third, uses the Taylor expansion:
\[ e' = 1 + J + \frac{1}{2} J^2 + \ldots \]  

Using Eqs. (39) and (40), the permeate flux is calculated as a function of time:

\[ v_w(t) = \frac{v_{w0}}{\sqrt{1 + w_{cg} t}} \]  

which indicates that the transient behavior of the normalized flux, i.e., the permeate flux at a given time \( t \) divided by \( v_{w0} \) of Eq. (43), is solely controlled by the single parameter \( w_{cg} \) characterizing triplet fouling mechanisms.

### 4.3.3.5 Revisit to pair-combined fouling.

**Macromolecules and Solutes:** Flux decline due to the doublet fouling of macromolecules and solutes can be easily analyzed by considering a special case of section 4.2.3.4. In the absence of colloidal particles, the following limits are taken:

\[ a_p \rightarrow 0 \]  
\[ \phi_f \rightarrow 0 \]  
\[ \phi_c \rightarrow 0 \]

Then, \( w_{cg} \) can be simplified in this case as:

\[ w_g = \lim_{\text{nocolloids}} w_{cg} \rightarrow \frac{2}{\Psi_g} \frac{v_{w0}}{\delta_{g,0}} \]  

where

\[ \Psi_g = \frac{\phi_g - \phi_f}{\phi_f} \]  

\[ \delta_{g,0} = \frac{R_m}{\hat{R}_g(\phi_g) + \Delta \pi_f / \mu D_g} \]  

\[ \hat{R}_g(\phi_g) = \frac{g \phi_g \Omega_H(\phi_g)}{2a_m^2} \]
and

\[ D_g = \lim_{\text{nocolloids}} D_{cg} = D_0 \frac{1 - \varphi_g}{\tau_g} \]  

(54)

**Colloids and Solutes:** When the doublet fouling from colloids and solutes is the main flux decline mechanism, \( w_{cg} \) for this special case can be obtained by replacing, in Eqs. (50) – (54), the subscripts ‘\( g \)’, \( a_m \), and \( \varphi \) with the subscripts ‘\( c \)’, \( a_p \), and \( \phi \), respectively. Such as,

\[ w_c = \frac{2 \nu_{wo}}{\Psi_c \delta_{c,0}} \]  

(55)

where

\[ \Psi_c = \frac{\phi_c - \phi_f}{\phi_f} \]  

(56)

\[ \delta_{c,0} = \frac{R_m}{\hat{R}_c(\phi_c) + \Delta \pi_f / \mu D_c} \]  

(57)

\[ \hat{R}_c(\phi_c) = \frac{9 \phi_c \Omega_{\mu}(\phi_c)}{2a_p^2} \]  

(58)

and

\[ D_c = D_0 \frac{1 - \phi_c}{\tau_c} \]  

(59)

4.3.4 **Equivalent flux.**

To comparatively analyze the degree of the combined fouling, an equivalent flux needs to be defined as a flux inferred from the linear superposition of individual colloidal and organic fouling. Here, we name fluxes of colloidal, organic, and combined fouling as
\( v_c, v_g, \) and \( v_{cg} \), which are equal to Eqs. (8), (16), and (17), respectively, and suggest two forms of the equivalent flux, denoted in this study as strong and weak forms.

### 4.3.4.1 Strong form of the equivalent flux.

A strong form of the equivalent flux was originally proposed by Lee et al. [20] and Li and Elimelech [35] as the flux of colloidal fouling subtracted by the flux decline of organic fouling:

\[

v_{eq}^s = 1 - (1 - v_c) - (1 - v_g)
\]

\[

= v_c - (1 - v_g)
\]

\[

= v_c + v_g - 1 = v_{add}
\]

(60)

defined as the "additive flux" since two fouling mechanisms are added through permeate fluxes. In their experiments, \( v_g \) was smaller than \( v_c \) because the size of organic matter is at least one order of magnitude smaller than that of the colloids. Note that the specific cake resistance is inversely proportional to the square of particle size. The equivalent flux of Eq. (60) provides a good inferred insight of how two individual fouling phenomena are ideally associated. However, this expression is limited to a condition, \( v_c + v_g > 1 \), otherwise the strong form of Eq. (60), \( v_{eq}^s \), is negative as shown by Lee et al. [20].

### 4.3.4.2 Weak form of the equivalent flux.

Since all the experiments done by Lee et al. [20] and Li and Elimelech [35] were conducted under constant pressures, investigation of resistance change with respect to the filtration time provides more meaningful, quantitative analysis. However, comparing \( v_{cg} \) and \( v_{eq}^s \) provides a better foresight of how much the combined fouling is severer than the
equivalent fouling, stemming from the linear superposition of colloidal and organic fouling phenomena. In this light, we propose a new equivalent flux of "weak form" based on the resistance-in-series model combined with the osmotic pressure model such as:

\[ \nu_{eq} \equiv \frac{\Delta P - \Delta \pi_{m,eq}}{\mu R_{eq}} \quad (61) \]

In Eq. (61), the total equivalent resistance is written as

\[ R_{eq} = R_m + R_c + R_g \quad (62) \]

implying that the cake and gel layers are separately stratified on the membrane surface, and the equivalent osmotic pressure is proposed as

\[ \Delta \pi_{m,eq} = \Delta \pi_{m,c} + \Delta \pi_{m,g} - \Delta \pi_f \quad (63) \]

where the osmotic pressure sum of colloidal and organic fouling cases is subtracted by \( \Delta \pi_f \) because the contribution of the feed concentration is double-counted in \( \Delta \pi_{m,c} \) and \( \Delta \pi_{m,g} \). Eq. (63) indicates that, using van't Hoff’s equation, the equivalent concentration on the membrane surface is the feed concentration plus the sum of concentration increases from the feed concentration due to colloidal and organic fouling. Then, Eq. (61) is re-written as

\[ \frac{\Delta P - \Delta \pi_{eq}}{\nu_{eq}} = \mu(R_m + R_c + R_g) \]

\[ = \frac{\Delta P - \Delta \pi_{m,c}}{\nu_c} + \frac{\Delta P - \Delta \pi_{m,g}}{\nu_g} - \frac{\Delta P - \Delta \pi_f}{\nu_{w0}} \quad (64) \]

or

\[ \frac{1}{\nu_{eq}} = \frac{\alpha_c}{\nu_c} + \frac{\alpha_g}{\nu_g} - \frac{\alpha_f}{\nu_{w0}} \quad (65) \]
where

\[ \alpha_c = \frac{\Delta P - \Delta \pi_{m,c}}{\Delta P - \Delta \pi_{eq}} = \left[ 1 - \frac{\Delta \pi_{m,g} - \Delta \pi_f}{\Delta P - \Delta \pi_{m,c}} \right]^{-1} \]  

(66a)

\[ \alpha_g = \frac{\Delta P - \Delta \pi_{m,g}}{\Delta P - \Delta \pi_{eq}} = \left[ 1 - \frac{\Delta \pi_{m,c} - \Delta \pi_f}{\Delta P - \Delta \pi_{m,g}} \right]^{-1} \]  

(66b)

\[ \alpha_f = \frac{\Delta P - \Delta \pi_f}{\Delta P - \Delta \pi_{eq}} = \left[ 1 - \frac{\Delta \pi_{m,c} + \Delta \pi_{m,g} - 2\Delta \pi_f}{\Delta P - \Delta \pi_f} \right]^{-1} \]  

(66c)

The osmotic pressure differences in Eq. (66) can be roughly estimated using van’t Hoff’s equation, as follows,

\[ \Delta \pi_{m,c} \sim \Delta \pi_{m,g} = (\beta + R_{ob})R_g T C_f = (\beta + R_{ob})\pi_f \]  

(67)

where

\[ \beta = \frac{C_m - C_f}{C_f} \]  

(68)

which indicates the net increase of the concentration on the membrane surface relative to that in the feed stream. Using Eqs. (33) and (67), we approximate Eq. (66) as

\[ \alpha_f \approx 1 + 2\beta \hat{\pi}_f \left[ 1 + (2\beta + R_{ob})\hat{\pi}_f \right] \approx 1 + 2\beta \hat{\pi}_f \]  

(69a)

\[ \alpha_c \approx 1 + \beta \hat{\pi}_f \left[ 1 + (2\beta + R_{ob})\hat{\pi}_f \right] \approx 1 + \beta \hat{\pi}_f \]  

(69b)

\[ \alpha_g = \alpha_c \]  

(69c)

where \( \hat{\pi}_f = \pi_f / \Delta P \). Note that the effect of observed rejection, \( R_{ob} \), is included only in the second order terms of Eq. (69).

The weak form of the equivalent flux is finally calculated as

\[ \frac{1}{v_{eq}} = \left( \frac{1}{v_c} + \frac{1}{v_g} - \frac{1}{v_{w0}} \right) \left[ 1 + \beta \hat{\pi}_f \right] - \frac{\beta \hat{\pi}_f}{v_{w0}} \]  

(70)
which assumes that the degrees of concentration polarization in colloidal and organic fouling are of similar values, and the feed osmotic pressure is much smaller than the trans-membrane pressure. In typical NF/RO operation, the concentration on the membrane surface is controlled so as not to exceed twice the feed concentration, i.e., \( \beta \leq 1 \). For low concentration of solute ions in feed water, \( \beta \hat{\pi} \), is almost negligible, then Eq. (70) becomes

\[
\frac{1}{v_{eq}} = \frac{1}{v_c} + \frac{1}{v_g} - \frac{1}{v_{w0}} \tag{71}
\]

which provides the maximum value of equivalent flux, \( v_{eq} \), of weak form by neglecting the osmotic pressure effects of solute ions due to a low rejection of the NF membrane (through \( \beta \)). The validity of Eqs. (70) and (71) can be mathematically checked as follows. If colloidal and organic fouling phenomena are negligible, then \( v_c \) and \( v_g \) reach \( v_{w0} \), so does \( v_{eq} \). On the other hand, if \( v_c \) or \( v_g \) is close to zero due to very severe fouling, then the right-hand-side of Eqs. (70) and (71) diverges, indicating that \( v_{eq} \) in the left-hand side converges to zero.

The equivalent flux, herein after, indicates its weak form of Eq. (71) while the strong form refers to the additive flux of Eq. (60). The combined flux represents the permeate flux of combined fouling due to colloids and macromolecules in NaCl solution.

### 4.4 Materials and Methods

#### 4.4.1 NF membrane.

A thin-film composite NF membrane was used (NF270, FilmTec Corp., Minneapolis, MN) for dead-end filtration. Membrane samples were cut to 76mm in
diameter and stored in deionized water at 4°C, with water replaced regularly. Membrane zeta potential was determined as \(-23.6 \pm 1.5\) mV from streaming potential measurements using an electrokinetic analyzer (Zeta CAD, CAD Instrumentation, Les Essarts le Roi, France). Measurements were conducted under solution conditions similar to those used in the dead-end filtration experiments in the absence of macromolecules and colloids.

4.4.2 Model foulants.

The model organic foulants used were bovine serum albumin (BSA), sodium alginate derived from brown algae, and dextran from \textit{Leuconostoc mesenteroides} (Sigma-Aldrich, St. Louis, MO), of which molecular weights are \(\sim 66, 10^{-6}\), and \(9-11\) kDa, respectively. Stock solutions were prepared by dissolving the powered organic compound in deionized water through vigorous mixing, and then stored in clean glass bottles at 4°C in dark. Commercial colloidal silica, Snowtex- XL (ST-XL, Nissan Chemical America Corp., Houston, TX) was used as the model colloidal foulant. Surface zeta potential and hydrodynamic diameter of the model foulants were characterized by electrophoretic mobility and dynamic light scattering (DLS) measurements using a Zetasizer Nano ZS (Malvern Instruments, Westborough, MA), as listed in Table 4-1. Detailed conditions can be found elsewhere [77].

4.4.3 Dead-end filtration experiments.

Fouling and chemical cleaning experiments were conducted in a bench-scale dead-end filtration system shown schematically in Fig. 4-5. The experimental set-up is described in detail elsewhere [15]. Three stainless steel reservoirs were used for the three
respective stages of the experiment (compaction, conditioning, and fouling). During the compaction stage, the stirred cell was filled with deionized water and the membrane was compacted at 130 psi for two hours or until the permeate flux stabilized. Next, an electrolyte solution of 10mM NaCl was added to the cell from the corresponding reservoir. Membranes were conditioned in the background electrolyte solution with stirring and proper salt rejection of the membrane was verified for at least two hours. Prior to the start of the fouling phase, the initial permeate flux was adjusted to 22.0 ± 2 μm/sec for all experiments, with the applied pressure used to obtain this flux ranging from 90–110 psi. After the membrane was equilibrated with the electrolyte solution and a constant flux was established, stirring was terminated and flow from the third reservoir housing containing the foulant solution was initiated. The fouling phase lasted for three hours.

4.5 Results

Figs. 4-6 – 4-8 show the flux decline behavior during the dead-end filtration of feed streams containing colloids-alone, macromolecules-alone, and both colloids and macromolecules, respectively, in 10 mM NaCl solutions. Three different macromolecules, BSA, alginate, and dextran, were used for the combined fouling experiments with STXL as a model colloid. To compare the theoretical prediction and experimental observations, the volume fractions of colloidal cake and macroscopic gel layers (i.e., $\phi_c$ and $\phi_g$, respectively) were calculated for the best fits to measured fluxes. Foulant properties and experimental conditions, employed for simulations, are listed in Table 4-1 and 4-2, respectively.
4.5.1 Colloids alone: Doublet fouling of colloids-alone in NaCl solution.

Colloidal filtration of STXL particles are shown in Figs. 4-6 – 4-8 with hollow square symbols, where excellent agreement is achieved between theoretical analysis and experimental observation using the random close packing ratio for the cake volume fraction, i.e., \( \phi_c = 0.64 \) [110-112]. The electrostatic double layer repulsion due to the colloidal zeta potential of \( \zeta = -37.90 \) mV seems to be effectively screened out by the ionic strength of \( C_r = 10^{-2} \) M NaCl, and therefore the behavior of STXL particles is similar to that of (non-interacting) hard spheres in terms of their packing behavior.

4.5.2 Macromolecules alone: Doublet fouling of organics-alone in NaCl solution.

As shown in Fig. 4-6, the transient flux decline behavior of the BSA-alone case is not successfully modeled using a single value of \( \phi_g \). During the first hour of filtration, the model prediction with \( \phi_g = 0.32 \) agrees well with the experimental observation; however, after two hours of filtration, \( \phi_g = 0.39 \) better describes the transient behavior. This suggests that the BSA-gel structure is compressed due to softness and/or eccentricity of BSA molecules [113].

Unlike BSA macromolecules, alginites and dextrans do not undergo (noticeable) structural compression in the course of gel formation/growth as shown in Fig. 4-7 and 4-8, respectively. The transient flux decline behaviors of the alginate and dextran fouling are well fitted using constant values of gel volume fraction, \( \phi_g = 0.35 \) and 0.23, respectively, indicating alginate forms a denser gel layer.
4.5.3 Combined fouling: Triplet fouling of colloids and macromolecules in NaCl solution.

4.5.3.1 The additive flux: the equivalent flux of strong form.

Plots with hollow triangular symbols in Figs. 4-6 – 4-8 show the experimental additive flux calculated using individually measured fluxes of STXL-alone and macromolecules (BSA, alginate, and dextran)-alone cases, based on the definition in Eq. (60). The theoretical additive flux of the STXL-BSA system of Fig. 4-6 with $\varphi_g = 0.32$ over predicts the experimental additive flux due to the BSA-gel compression, but those of STXL-alginate and STXL-dextran systems of Figs. 4-7 and 4-8, respectively, well mimics the experimental observations along the entire filtration duration.

In Fig. 4-6, flux prediction of the additive fouling with $\varphi_g = 0.32$ reasonably mimics the experimental results during the first hour but deviates noticeably from the measurements after the second hour due to the BSA-gel compression. At the later stage, the experimental additive flux becomes lower than that of the combined fouling. The fitted value of $\varphi_g = 0.32$ better predicts the initial stage of the BSA-alone case and the later stage of the combined fouling phenomena, although it fails to predict the experimental additive flux after the second hour. Based on the additive flux, one can conclude that the combined fouling could be milder than the additive sum of individual fouling of STXL-alone and BSA-alone cases. This misconception initially comes from the compressibility of the gel layer but primarily originates from the definition of the additive flux of Eq. (60).
As shown in Figs. 4-7 and 4-8, theoretical additive fluxes of alginate and dextran fouling match better with the experimental observations than that of the BSA-alone case shown in Fig. 4-6. This is because of the good prediction of the macromolecular doublet fouling using constant gel volume fractions of \( \varphi_g = 0.35 \) and 0.23 for alginites and dextrans, respectively. Experimental additive fluxes, shown in Figs. 4-7 and 4-8, are always lower than the measured fluxes of combined fouling due to the mixture of STXL-alginate and STXL-dextran, respectively. As noted above, this phenomenon does not indicate that a bi-mixture of two foulants mitigates the combined fouling, which appears to be less than the superposition of two individual fouling phenomena in terms of the additive flux. In Figs. 4-6 – 4-8, crossover between the experimental additive flux and theoretical combined flux does not represent an important physical implication, but it naturally occurs since the additive flux will eventually reach zero.

4.5.3.2 The equivalent flux (of the weak form).

Due to the low slat rejection of the NF membrane used, Eq. (71) is used to estimate the equivalent flux (of the weak form), which provide the maximum value from neglecting effects of NaCl osmotic pressure. The difference between theoretical and experimental equivalent fluxes, shown in Fig. 4-6 with solid triangular symbols and a solid line, respectively, becomes larger as the filtration proceeds due to the structural compression of the BSA-gel layer, but much less than that between theoretical and experimental additive fluxes. On the other hand, Figs. 4-7 and 4-8 show good agreement between the theoretical and experimental equivalent fluxes of STXL with alginate and dextran, respectively, indicating solidity of the alginate and dextran gel layers. Because the theoretical equivalent flux calculated using Eq. (71) neglects the osmotic pressure of
NaCl, it implies that STXL-cake and BSA-gel layers are vertically stratified on the membrane surface, one above the other and vice versa.

4.5.3.3 The combined flux.

The theoretical prediction of the combined flux does not require a new fitting process but uses two values of $\phi_c$ and $\phi_g$, previously determined by analyzing doublet fouling of colloids-alone and macromolecules-alone cases in NaCl solutions. Due to the higher sensitivity of cake resistance to the volume fraction than the thickness, a higher volume fraction of the combined layer (i.e., $\phi_c + \phi_g$) provides the combined flux lower than the equivalent flux using the same $\phi_c$ and $\phi_g$.

Fig. 4-6 shows the combined flux due to STXL and BSA in the NaCl solution, which is modeled with $\phi_c = 0.64$ and $\phi_g = 0.32$ (instead of $\phi_g = 0.39$). The current theory underpredicts the transient permeate flux of the BSA-STXL combined fouling for the first two hours, which indicates that the actual resistance occurring during the experiment is less than what is predicted using Eq. (18). The specific resistance of the combined layer presumes constant values of $\phi_c$ and $\phi_g$ in Eq. (20), which seems to be incorrect (at least) at the initial stage of the filtration. This implies that STXL particles and BSA molecules are not instantaneously mixed with each other when STXL particles form the first few deposit layers on the membrane surface. STXL particles, which are bigger and heavier than BSA molecules, can deposit earlier, and BSA molecules may gradually penetrate into and fill in the local interstitial gaps within the cake layer of the pre-deposited colloids. Due to the small void fraction of 36% within the colloidal swarm, the penetration of the macromolecules is a limiting factor that governs the initial rate of the
permeate flux decline. The gel concentration within the combined layer can be lower than that of the individual organic layer. However, in the later stage of the combined fouling, the theoretical prediction and experimental observation are well superimposed upon each other. The local gel structure formed within the interstitial spaces of the colloidal swarm is incompressible and therefore generates a constant specific resistance of the combined layer. This is because the colloidal particles, about $10^3$ times bigger than macromolecules in volume, provide a geometrically confined environment and induce only a minute compression of local gel structures.

Fig. 4-7 shows that, unlike BSA-STXL combined fouling, the experimental combined flux of alginate and STXL is closer to its theoretical equivalent flux. This indicates that the alginate volume fraction within the STXL cake layer is less than 0.35, which fits the flux decline of the alginate doublet fouling. Fig. 8 also shows a similar trend that the experimental combined flux is larger than the theoretical combined flux, but less than the equivalent flux. The volume fraction of dextran-gel within STXL cake layer is less than $\varphi_s = 0.23$, which was obtained from the analysis of dextran doublet fouling in the NaCl solution.

4.5.4 Comparative analysis.

By comparing Figs. 4-6 and 4-8, one can see that the net interaction between BSA and STXL is more attractive (or less repulsive) than those between alginate and STXL and between dextran and STXL. A stronger repulsive interaction between colloids and macromolecules can make the experimental combined flux closer to the theoretical equivalent flux. The theoretical combined flux will better mimic the experimental
measurement of the combined fouling if an attractive interaction, which may cause macromolecular adsorption on the colloidal surfaces, dominates between colloids and macromolecules. The theoretical estimations of combined and equivalent fouling phenomena using Eqs. (48) and (71), generates the lower and upper boundaries, respectively, of the experimentally observed flux of the combined fouling of which resistance is less than that of a well-mixed colloids-macromolecules structure, but greater than that of the stratified layer. It is worth noting that the experimental flux of combined fouling is always lower than theoretical equivalent flux and greater than the theoretical combined flux. The degree of the combined fouling in the NF filtration primarily relies on net mutual interactions between colloids and macromolecules and deformability of macromolecules.

4.6 Conclusions

A novel theory is developed on the basis of the sphere-in-cell model to analyze the combined fouling of colloids, macromolecules, and solute ions. The current model unifies singlet fouling due to individual foulants, doublet fouling due to paired foulants, and triplet fouling due to a mixture of the three foulants. The special case of this model includes cake-enhanced osmotic pressure model and resistance-in-series model for binary suspensions. The hydrodynamic model of a swarm of composite spheres [103], i.e., mono-dispersed solid spheres with a uniformly porous shell, is used to predict the specific resistance of the combined layer, i.e., colloidal cake layer of which interstitial spaces are filled with macromolecules.
Volume fractions of colloidal cake and macromolecular gel layers in the NaCl solutions, i.e., $\phi_e$ and $\varphi_g$, are obtained by fitting dead-end filtration data and used to predict the flux decline of the combined fouling. The theory primarily assumes a complete and instantaneous mixing of colloids and macromolecules, which form the combined deposit layer. Diffusive tortuosity of the combined layer is calculated as a product of those of the colloidal cake and gel layer. The equivalent flux is categorized into the strong and weak forms, which refer to the additive flux originally proposed by Lee et al. [20] and Li and Elimelech [35] and the permeate flux corresponding to the stratified structure of colloidal and gel layers, respectively.

The internal structure of the colloidal (STXL) cake layer appears to be the random close packing with the specific volume fraction of 0.64. The dead-end filtration of BSA shows that BSA-gel layer is gradually compressed as the filtration proceeds while no compression effects are shown in alginate and dextran dead-end filtrations. The additive flux reasonably predicts the combined flux only at the beginning of the filtration but become noticeably lower than the combined flux after about two hours. This is because the additive flux will be negative after it passes zero while the equivalent flux will gradually converge to zero from the positive.

The current theory provides two novel equations: one for the equivalent flux of the weak form of Eq. (48) and the other for the combined flux of Eq. (71), which play roles of the upper and lower bounds of the experimental flux of the combined fouling. The internal structure of the combined fouling layer, influenced by pair-interactions between foulants, is between completely mixed and vertically stratified structures of colloidal cake and macromolecular gel layers.
Table 4-1 Physical properties and feed conditions of four foulants. The mass concentration of silica was 100 mg/L and those of three organic foulants were 20 mg/L.

<table>
<thead>
<tr>
<th></th>
<th>Silica</th>
<th>BSA</th>
<th>Alginate</th>
<th>Dextran</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed volume fraction ($10^{-5}$)</td>
<td>4.35</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Hydrodynamic radius (nm)</td>
<td>30.4</td>
<td>2.56</td>
<td>3.45</td>
<td>2.16</td>
</tr>
<tr>
<td>Zeta potential (mV)</td>
<td>$-37.9 \pm 0.4$</td>
<td>$-20.7 \pm 0.9$</td>
<td>$-45.0 \pm 1.2$</td>
<td>$-7.2 \pm 1.5$</td>
</tr>
<tr>
<td>Solid density (g/cm$^3$)</td>
<td>2.3</td>
<td>(≈) 1.0</td>
<td>(≈) 1.0</td>
<td>(≈) 1.0</td>
</tr>
</tbody>
</table>

(The solid densities of macromolecules are assumed to be approximately equal to that of water.)

Table 4-2 Experimental conditions used for simulations.

<p>| | |</p>
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl feed concentration</td>
<td>$C_f = 0.01M$</td>
</tr>
<tr>
<td>NaCl Diffusivity</td>
<td>$D_0 = 1.611 \times 10^{-9}$ m$^2$/s</td>
</tr>
<tr>
<td>Membrane resistance</td>
<td>$R_m = 1.98 \times 10^{13}$ m$^{-1}$</td>
</tr>
<tr>
<td>Water viscosity</td>
<td>$\mu = 1.0 \times 10^{-3}$ kg/m · s</td>
</tr>
<tr>
<td>Initial flux</td>
<td>$v_{w0} = 22.0 \mu$m/s</td>
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Figure 4-1 Schematics of (a) colloidal cake layer, (b) macromolecular gel layer, and (c) solute concentration polarization layer.

Figure 4-2 Equivalent profiles of ion concentration shown with solid lines: when (a) the solute concentrations on the membrane surface, $C_m$, and (b) the thicknesses of concentration polarization, $\delta_s$, are assumed to be equal in the presence and absence of the colloidal cake layer. Dotted lines indicate the real solute concentration profile with the colloidal cake layer: the constant feed concentration $C_f$ in the bulk phase ($y \geq \delta_s$) and increasing $C(y)$ toward the membrane surface due to the concentration polarization.
Figure 4-3 A cell model of a binary mixture of colloidal particles (big spheres) of radius $a_p$ and macromolecules (small spheres) of radius $a_m$. The merged cake layer composed of both colloidal particles and macromolecules is mapped on to a single spherical cell containing a colloid and $n_m$ macromolecules. The cell has the radius of $b$, and the tangential stress is free on the surface [17, 103].
Figure 4-4 Solute diffusion in (a) a free space, (b) the gel layer, and (c) the combined gel-cake layer. The
diffusive flux along the length $\Delta y$ due to the concentration difference $\Delta C = C_2 - C_1$ is
$J_i = D_i \frac{\partial C}{\partial y} = D_i \frac{\Delta C}{\Delta y}$ where the subscript $i$ applies to the three cases of (a), (b), and (c): (a) $D_a = D_0$ because the solute diffusion occurs in a free space, (b) $D_b = D_0 \frac{\varepsilon_g}{\tau_g}$ because the hindered diffusion occurs in the void space of the gel layer of porosity $\varepsilon_g$ when the solutes take tortuous routes of tortuosity $\tau_g$, and (c), in the same way, $D_c = D_b \frac{\varepsilon_c}{\tau_c} = D_0 \frac{\varepsilon_g \varepsilon_c}{\tau_g \tau_c}$. The gel layer of case (b) can be considered as a uniform medium through which solutes can perform the diffusive motions (being hindered as much as $D_0 \left(1 - \frac{\varepsilon_g}{\tau_g}\right)$) with the effective diffusivity of $D_b$. The expression of $D_b$ is easily extended to develop that of $D_c$, which represents the solute diffusion that is hindered microscopically by local gel structure of porosity $\varepsilon_g$ and macroscopically by global cake structure of porosity $\varepsilon_c$. 

![Diagram showing solute diffusion in (a) a free space, (b) the gel layer, and (c) the combined gel-cake layer.]
Figure 4-5 Schematic of the dead-end filtration unit.
Figure 4-6 Flux decline behaviors of colloids (STXL)-alone, macromolecules (BSA) - alone, additive fouling (of short-term and long-term), equivalent fouling, and combined fouling, commonly in $10^{-2}$ mM NaCl solutions. The volume fraction of the colloidal cake layer is chosen as the random close packing ratio of $\phi_c = 0.64$, and that of macromolecular gel is assumed to be $\phi_g = 0.32$ and $\phi_g = 0.39$ for the initial and later stages of filtration respectively. The permeate fluxes of the additive and equivalent fouling are calculated using Eqs. (60) and (71), respectively. The calculation of theoretical combined flux uses $\phi_c = 0.64$ and $\phi_g = 0.32$. 
Figure 4-7 Flux decline behaviors of colloids (STXL)-alone, macromolecules (alginate)-alone, additive fouling, equivalent fouling, and combined fouling, commonly in $10^{-2}$ mM NaCl solutions. The volume fractions of the colloidal cake and macromolecular gel layers are fitted as $\phi_c = 0.64$ and $\phi_g = 0.35$, respectively. The theoretical fluxes of the additive and equivalent fouling are calculated using Eqs. (60) and (71), respectively.
Figure 4-8 Flux decline behaviors of colloids (STXL)-alone, macromolecules (dextran)-alone, additive fouling, equivalent fouling, and combined fouling, commonly in $10^{-2}$ mM NaCl solutions. The volume fractions of the colloidal cake and macromolecular gel layers are fitted as $\phi_c = 0.64$ and $\varphi_g = 0.23$, respectively. The permeate fluxes of the additive and equivalent fouling are calculated using Eqs. (60) and (71), respectively.
5. Conclusions

The goal of this research was to provide a mechanistic study the combined fouling of a complex solution of inorganic colloids and organic macromolecules. Using four model organic foulants and one model colloidal foulant, the three mechanisms examined experimentally (change in fouling layer structure, hindered back diffusion of solutes and modified foulant characteristics based on foulant-foulant interactions) were shown to contribute to the synergism observed during combined fouling. The extent of the synergy, however, strongly depends on the specific molecular characteristics of the organic foulant. Absorptive interaction between organic and colloidal foulants is shown through the model organic foulant BSA to be a complex mechanism capable of the greatest synergism. Additionally, interaction between the organic foulant and membrane surface can modify initial fouling behavior. The effect of cake layer structure appears to be a time dependent mechanism, as significant foulant accumulation on the membrane surface is first necessary. After time, cake layer structure changes to provide greater resistance and even further enhanced flux decline. It is necessary that flux decline models incorporate these mechanisms in order to accurately predict flux decline of solutions most closely representing natural and waste waters.

Preliminary modeling work was done to incorporate changes in cake layer structure and the interactions between foulants that may occur during complex filtration by modeling a merged fouling layer on the basis of a sphere-in-cell model. This method models the specific fouling layer resistance through a swarm of mono-dispersed solid spheres with a uniformly porous shell i.e., colloidal cake layer of which interstitial spaces are filled with macromolecules. The theory primarily assumes a complete and
instantaneous mixing of colloids and macromolecules, which form the combined deposit layer. Diffusive tortuosity of the combined layer is calculated as a product of those of the colloidal cake and gel layer. Fitted volume fractions of the colloid and organic in the fouling layer (\( \phi_c \) and \( \varphi_g \)) explain experimental results well and reveal insight into both simple and complex fouling layer structures that lead to changes in resistance and flux decline over time. While the STXL layer is fitted through close random packing volume fraction (0.64), the dead-end filtration of BSA shows that the BSA-gel layer gradually compresses as the filtration proceeds. No compression effects are shown in filtrations involving alginate and dextran. The assumption of a completely mixed fouling layer during complex filtration may be too simplifying an assumption to make during the initial stages of fouling when fouling is caused by preferential accumulation of heavier particles. Therefore, the internal structure of the combined fouling layer, influenced by pair-interactions between foulants, is between completely mixed and vertically stratified structures of colloidal cake and macromolecular gel layers.
6. Future Work

Many more experiments can be performed on this topic in order to reveal more about the combined fouling mechanisms already discussed. First and foremost, performing similar cross-flow and dead-end filtration experiments under different salt conditions (including varying both concentration and type of salt ion) will more accurately represent real natural waters. In particular, it would be best to add divalent ions (such as Mg$^{2+}$ or Ca$^{2+}$) as these ions are present in most waters and fouling behavior has been shown to change significantly in their presence.

Another facet of this research that could be explored is imaging the fouled membranes in order to directly investigate the fouling layer structure. Previous studies have developed a successful resin embedding protocol for autopsyng fouled membranes using transmission electron microscopy (TEM) [114, 115]. A similar approach can be used to explore where in the fouling layer the colloid and organic particles are positioned in order to gain a better understanding for how resistance of combined layers should be calculated.

Also, in this study emphasis is placed on the interaction between foulants with respect to the zeta potential measurements of combined solutions and the QCM-D measurements between a silica surface and organics in solution. In addition to these interactions, the membrane-particle interactions are extremely important in determining fouling potential of a species. Synthesizing a "membrane coated" quartz crystal for QCM-D purposes will enable the study of the interaction between foulant particles and the membrane surface. This measurement may be more useful quantifying these interactions than the streaming potential measurement alone. A similar result can be
achieved using atomic force microscopy (AFM) in order to quantify these interactions. Colloid and organic coated colloid cantilever probes can be constructed in order to directly measure the forces between the membrane surface and each foulant.

In addition to the extended experimental work recommended above, further theoretical modeling that incorporates more complicated hydrodynamic conditions (such as cross-flow filtration) will also be useful for understanding real-life filtration schemes. Terms that directly describe the complicated foulant-foulant interactions can also provide insight into fouling phenomena.
List of References


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Appendix I: Cross-flow Filtration Data

Complete data for the cross-flow filtration experiments presented in Chapter 3.
Appendix II: Salt Rejection Data

Complete salt rejection data for the cross-flow experiments presented in Chapter 3.
Appendix III: Zeta Potential and Particle Size Data

Complete zeta potential and particle size data for each solution combination over a range of pH (4 – 10). Data points are the average of five measurements and appropriate standard deviation error bars.